

TITLE OF THE INVENTION

METHOD OF INCREASING SPEED OF SILVER HALIDE COLOR  
PHOTOSENSITIVE MATERIAL

CROSS-REFERENCE TO RELATED APPLICATIONS

5           This application is based upon and claims the  
benefit of priority from the prior Japanese Patent  
Applications No. 2001-358036, filed November 22, 2001;  
and No. 2002-138621, filed May 14, 2002, the entire  
contents of both of which are incorporated herein by  
10           reference.

BACKGROUND OF THE INVENTION

1. Field of the Invention

          The present invention relates to a method for  
obtaining images with an increased speed using a silver  
15           halide color photosensitive material.

2. Description of the Related Art

          In the field of silver halide color photosensitive  
materials, it has been a problem to be solved for a  
great many years to enhance speed without damaging  
20           graininess. In general, the speed depends on the grain  
size of a silver halide emulsion. The larger the grain  
size of the emulsion, the more the speed increases.  
However, since the graininess deteriorates with  
increase of the size of a silver halide grain, the  
25           speed and graininess have a trade-off relationship. In  
this field, it is the most basic and important problem  
to be solved in improving the image quality of a

photosensitive material, to increase speed without deteriorating graininess.

A technique of increasing speed without deteriorating graininess by containing, in a silver halide photosensitive material, a compound having a minimum of three hetero atoms which do not react with an oxidized color developing agent, has been disclosed, for example, in the publication of Jpn. Pat Appln. KOKAI Publication No. (hereinafter referred to as JP-A-) 2000-194085.

However, although it has been found that speed is increased by using the method described in the above publication, the effect thereof is insufficient, and that there are also side effects caused by the addition of such a compound. If the compound coexists with a silver halide emulsion, an undesirable mutual action occurs, and undesirable time-lapse deterioration at the time of storage of a coating liquid or a photosensitive material occurs.

#### BRIEF SUMMARY OF THE INVENTION

As a result of studies in searching for a more advantageous effect and in solving the problem, the inventors arrived at a method of preferably increasing the speed by a compound represented by general formula (M) or general formula (C). It is presumed that a compound having properties of adsorbing on the surface of an emulsion grain is advantageous for the purpose,

and the compound of general formula (M) or (C) of the present invention is superior, in this point, to the compound described in the publication JP-A-2000-194085, although details of the mechanism are unknown. It is also presumed that it is desirable for the compound to be added to have moderate reactivity with an oxidized color developing agent, in view of the properties of inhibiting undesirable latent image bleaching during development.

The compound of general formula (M) or (C) of the present invention is a coupler having reactivity with an oxidized color developing agent. The present invention provides a method of improving speed/graininess of a photosensitive material using this compound. Thus, the present invention is different from the structure of the invention disclosed in the publication of JP-A-2000-194085 describing a photosensitive material whose speed is enhanced by using a compound which does not react with an oxidized color developing agent.

It is an object of the present invention to provide a method of increasing speed of a silver halide color photosensitive material without deteriorating image quality such as graininess.

The inventors have found that the above problem can be solved by using the compound represented by general formula (M) or (C) described later. They

believe that the mechanism of the action of the compound of the present invention exerts an effect by eliminating speed loss at the time of development. From analytical results, it is presumed that the compound of the present invention weakens, during development, the ability of a sensitizing dye to adsorb on an emulsion surface, and activates a latent image which is not usually developed, thereby increasing the number of development initiating points. The sensitizing dye exists in an emulsion grain surface at the time of photography and is indispensable to increase optical speed. However, the sensitizing dye sometimes inhibits the oxidized color developing agent from reacting with a latent image at the time of development. The compound of the present invention, when it is used by emulsification dispersion, exists in oil droplets at the time of photography. If the pH of the developing solution is high, the compound dissociates, i.e., elutes from the oil droplet, and acts on the emulsion grain surface. It has been found that in order to make effective use of the above property, it is effective to set the pKa of the compound at a value in the vicinity of, or less than, the pH of the developing solution. By providing the present invention with such a property, a more advantageous effect can be obtained than by the compound disclosed in the publication of

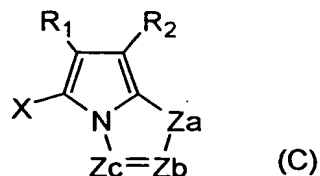
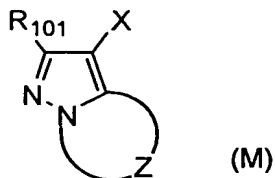
JP-A-2000-194085. The reduction in the undesired mutual action with an emulsion can be realized at the time of manufacture or storage of the photosensitive material. The compound of the present invention is  
5 designed as a coupler in order to provide the compound with the above property, and its coloring property can also be utilized as a part of a main coupler.

~~As a result~~ As a result of further studies, it has been found that the use of the above compound leads to enhancement  
10 of the reactivity of a latent image on the emulsion surface at the time of development, and, the reactivity with the oxidized color developing agent. However, latent image bleaching due to oxidation easily occurs. It has therefore been found that if the pAg-increasing  
15 property of the compound of the present invention is too high, latent image bleaching occurs simultaneously, and thus the desired effect of increasing the number of development initiating points is suppressed.

It has also been found that the above coupler  
20 structure brings about an effect of increasing the number of development initiating points, and a coloring dye obtained after reaction with the oxidized color developing agent does not have such an effect, thus it is more preferable if the color forming property of the  
25 coupler of the present invention is not too high.

That is, the present invention provides the following method.

(1) A method of increasing speed of a silver halide color photosensitive material by at least one type of a compound represented by the following general formula (M) or general formula (C):



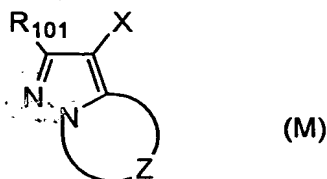
In formula (M),  $R_{101}$  represents a hydrogen atom or substituent. Z represents a group of non-metallic atoms required to form a 5-membered azole ring containing 2 to 4 nitrogen atoms. The azole ring may have a substituent (including a fused ring, i.e., an aromatic ring such as a benzene ring may be fused to the azole ring). X represents a hydrogen atom or substituent.

15 In formula (C),  $Z_a$  represents  $-NH-$  or  $-CH(R_3)-$ , and  $Z_b$  and  $Z_c$  independently represent  $-C(R_4)=$  or  $-N=$ .  $R_1$ ,  $R_2$  and  $R_3$  independently represent an electron attractive group having a Hammett constant  $\sigma_p$  value of 0.2 to 1.0.  $R_4$  represents a hydrogen atom or substituent. If there are two  $R_4$ s in the formula, they may be the same or different. X represents a hydrogen atom or substituent.

(2) The method of increasing speed of a silver halide color photosensitive material according to (1), wherein, in the formula (M), the total number of carbon atoms of the substituents on the azole ring, including

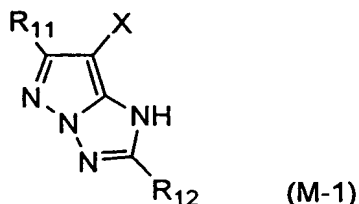
R<sub>101</sub>, X and Z, is from 13 to 60.

(3) The method of increasing speed of a silver halide color photosensitive material according to (1) or (2), wherein the method comprises adding, to the silver halide color photosensitive material, the compound represented by the general formula (M):



In formula (M), R<sub>101</sub> represents a hydrogen atom or substituent. Z represents a group of non-metallic atoms required to form a 5-membered azole ring containing 2 to 4 nitrogen atoms. The azole ring may have a substituent (including a fused ring). X represents a hydrogen atom or substituent.

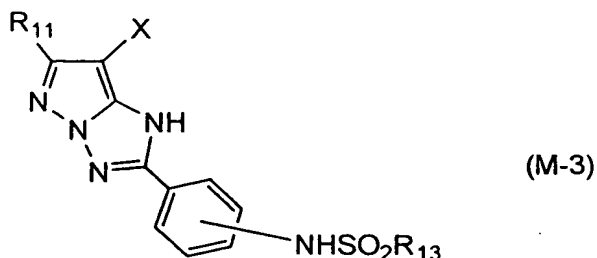
(4) The method of increasing speed of a silver halide color photosensitive material according to (3), wherein the general formula (M) is represented by general formula (M-1):



In the formula, R<sub>11</sub> and R<sub>12</sub> independently represent a substituent. X represents a hydrogen atom or substituent.

(5) The method of increasing speed of a silver halide color photosensitive material according to (3),

wherein the general formula (M) is represented by  
general formula (M-3):



In the formula,  $R_{11}$  and  $R_{13}$  independently  
5 represent a substituent. X represents a hydrogen atom  
or substituent.

(6) The method of increasing speed of a silver  
halide color photosensitive material according to any  
one of (1) to (5), wherein the addition of the compound  
10 represented by the general formula (M) or (C) changes a  
film  $pAg$  ( $\Delta pAg_F$ ) of the silver halide color  
photosensitive material by 0 to 0.3.

(7) The method of increasing speed of a silver  
halide color photosensitive material according to any  
15 one of (1) to (6), wherein the compound represented by  
the general formula (M) or (C) has a  $pK_a$  value of 6.0  
to 8.4.

(8) The method of increasing speed of a silver  
halide color photosensitive material according to any  
20 one of (1) to (7), wherein the compound represented by  
the general formula (M) or (C) has a reactivity (CRV)  
with an oxidized color developing agent of 0.01 to 0.1.

(9) The method of increasing speed of a silver  
halide color photosensitive material according to any



one of (1) to (8), wherein the method comprises adding, to a red-sensitive silver halide emulsion layer of the silver halide color photosensitive material, the compound represented by the general formula (M) or (C).

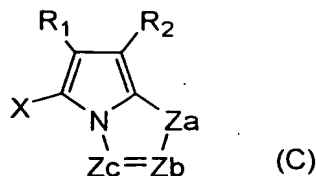
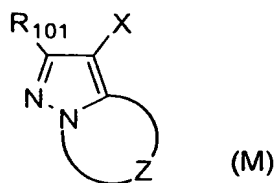
5           (10) The method of increasing speed of a silver halide color photosensitive material according to any one of (1) to (9), wherein the method comprises adding, to a blue-sensitive silver halide emulsion layer of the silver halide color photosensitive material, the  
10       compound represented by the general formula (M) or (C).

          (11) The method of increasing speed of a silver halide color photosensitive material according to any one of (1) to (10), wherein a layer of the  
          photosensitive material containing tabular grains  
15       having an average aspect ratio of 8 or more, contains at least one compound represented by the general formula (M) or general formula (C).

          Additional objects and advantages of the invention will be set forth in the description which follows, and  
20       in part will be obvious from the description, or may be learned by practice of the invention. The objects and advantages of the invention may be realized and obtained by means of the instrumentalities and combinations particularly pointed out hereinafter.

25           DETAILED DESCRIPTION OF THE INVENTION

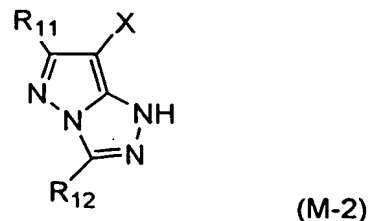
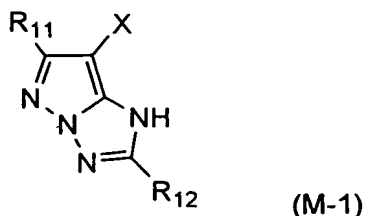
          The compound represented by general formula (M) or (C) will be described below.



In formula (M),  $R_{101}$  represents a hydrogen atom or substituent. Z represents a group of non-metallic atoms required to form a 5-membered azole ring containing 2 to 4 nitrogen atoms. The azole ring may have a substituent (including a fused ring). X represents a hydrogen atom or substituent.

In formula (C),  $Z_a$  represents  $-NH-$  or  $-CH(R_3)-$ , and  $Z_b$  and  $Z_c$  independently represent  $-C(R_4)=$  or  $-N=$ .  $R_1$ ,  $R_2$  and  $R_3$  independently represent an electron attractive group having a Hammett constant  $\sigma_p$  value of 0.2 to 1.0.  $R_4$  represents a hydrogen atom or substituent. If there are two  $R_4$ s in the formula, they may be the same or different. X represents a hydrogen atom or substituent.

The compound of the present invention will be described in detail below. Of the skeletons represented by formula (M), preferable skeletons are 1H-pyrazolo[1,5-b][1,2,4]triazole and 1H-pyrazolo[5,1-c][1,2,4]triazole, which are represented by formula (M-1) and (M-2), respectively.



In the formula,  $R_{11}$  and  $R_{12}$  represent a

substituent. X represents a hydrogen atom or substituent.

The substituents  $R_{11}$ ,  $R_{12}$  and X in formula (M-1) or (M-2) will be described in detail.

5         $R_{11}$  preferably represents a halogen atom (e.g., chlorine atom, bromine atom, and fluorine atom), alkyl group (having 1 to 60 carbon atoms, e.g., methyl, ethyl, propyl, iso-butyl, t-butyl, t-octyl, 1-ethylhexyl, nonyl, cyclohexyl, undecyl, pentadecyl, n-hexadecyl, and 3-decanamidepropyl), alkenyl group (having 2 to 60 carbon atoms, e.g., vinyl, allyl, and oleyl), cycloalkyl group (having 5 to 60 carbon atoms, e.g., cyclopentyl, cyclohexyl, 4-t-butylcyclohexyl, 1-indanyl, and cyclododecyl), aryl group (having 6 to 60 carbon atoms, e.g., phenyl, p-tolyl, and naphthyl), acylamino group (having 2 to 60 carbon atoms, e.g., acetylamino, n-butanamide, octanoylamino, 2-hexyldecanamide, 2-(2',4'-di-t-amylphenoxy)butanamide, benzoylamino, and nicotinamide), sulfonamide group (having 1 to 60 carbon atoms, e.g., methanesulfonamide, octanesulfonamide, and benzenesulfonamide), ureide group (having 2 to 60 carbon atoms, e.g., decylaminocarbonylamino, and di-n-octylaminocarbonylamino), urethane group (having 2 to 60 carbon atoms, e.g., dodecyloxycarbonylamino, phenoxy carbonylamino, and 2-ethylhexyloxycarbonylamino), alkoxy group (having 1 to 60 carbon atoms, e.g., methoxy, ethoxy, butoxy, n-octyloxy, hexadecyloxy, and

methoxyethoxy), aryloxy group (having 6 to 60 carbon atoms, e.g., phenoxy, 2,4-di-t-amylphenoxy, 4-t-octylphenoxy, and naphthoxy), alkylthio group (having 1 to 60 carbon atoms, e.g., methylthio, ethylthio, butylthio, and hexadecylthio), arylthio group (having 6 to 60 carbon atoms, e.g., phenylthio, and 4-dodecyloxyphenylthio), acyl group (having 1 to 60 carbon atoms, e.g., acetyl, benzoyl, butanoyl, and dodecanoyl), sulfonyl group (having 1 to 60 carbon atoms, e.g., methanesulfonyl, butanesulfonyl, and toluenesulfonyl), cyano group, carbamoyl group (having 1 to 60 carbon atoms, e.g., N,N-dicyclohexylcarbamoyl), sulfamoyl group (having 0 to 60 carbon atoms, e.g., N,N-dimethylsulfamoyl), hydroxy group, sulfo group, carboxyl group, nitro group, alkylamino group (having 1 to 60 carbon atoms, e.g., methylamino, diethylamino, octylamino, and octadecylamino), arylamino group (having 6 to 60 carbon atoms, e.g., phenylamino, naphthylamino, and N-methyl-N-phenylamino), heterocyclic group (having 0 to 60 carbon atoms, preferably 3- to 8-membered, and more preferably, 5- to 6-membered heterocyclic group including a hetero atom, which forms a ring, selected from the group consisting of a nitrogen atom, oxygen atom, and sulfur atom, and more preferably, including a carbon atom as the ring-forming atoms in addition to the hetero atoms, e.g., a group indicated as an example of term X described

later), and an acyloxy group (having 1 to 60 carbon atoms, e.g., formyloxy, acetyloxy, myristoyloxy, and benzoyloxy).

5 Of the above, the alkyl group, cycloalkyl group, aryl group, acylamino group, ureide group, urethane group, alkoxy group, aryloxy group, alkylthio group, arylthio group, acyl group, sulfonyl group, cyano group, carbamoyl group, and ~~sulfamoyl~~ group include those having a substituent. Examples of the substituent are  
10 an alkyl group, cycloalkyl group, aryl group, acylamino group, ureide group, urethane group, alkoxy group, aryloxy group, alkylthio group, arylthio group, acyl group, sulfonyl group, cyano group, carbamoyl group and sulfamoyl group.

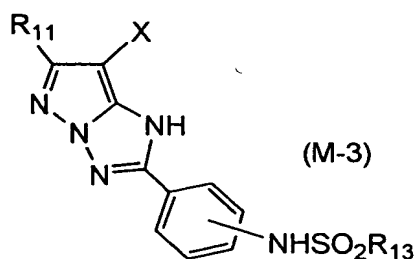
15 Of these substituents, preferable examples of  $R_{11}$  are an alkyl group, aryl group, alkoxy group, and aryloxy group. An alkyl group, alkoxy group and aryloxy group are more preferably. A branched alkyl group is especially preferable.

20  $R_{12}$  preferably represents the substituents as indicated for  $R_{11}$ . More preferable examples of the substituents are an alkyl group, aryl group, heterocyclic group, alkoxy group, and aryloxy group.

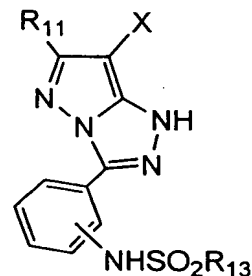
25  $R_{12}$  still more preferably represents a substituted alkyl group and substituted aryl group, and most preferably, a substituted aryl group. Compounds represented by general formulae (M-3) and (M-4) are

preferable.

In the general formula (M), the total number of carbon atoms of the substituents on the azole ring, including  $R_{101}$ , X and Z, is not particularly limited, but the total number is preferably from 13 to 60, and more preferably 20 to 50, in order to enhance the adsorption capacity of the compound represented by the general formula (M) to emulsion grains and to enhance the advantage in improving the speed/graininess ratio.



(M-3)



(M-4)

10

In the formula,  $R_{11}$  and X have the same meanings as those defined in general formulae (M-1) and (M-2).  $R_{13}$  represents a substituent. Examples of preferable substituents represented by  $R_{13}$  are the substituents enumerated above for  $R_{11}$ . Examples of more preferable substituents are a substituted aryl group, and a substituted or unsubstituted alkyl group. As the substituent in this case, the substituents enumerated above as examples of  $R_{11}$  are preferable.

20

X represents a hydrogen atom or substituent. Preferable examples of the substituents are those enumerated as examples of  $R_{11}$ . More preferable examples of the substituents represented by X are an alkyl group, alkoxycarbonyl group, carbamoyl group or a

group which leaves by reaction with an oxidized developing agent. Examples of the leaving group are a halogen atom (fluorine, chlorine, bromine, etc.), alkoxy group (ethoxy, methoxycarbonylmethoxy, carboxypropyloxy, methanesulfonylethoxy, perfluoropropoxy, etc.), aryloxy group (4-carboxyphenoxy, 4-(4-hydroxyphenylsulfonyl)phenoxy, 4-methanesulfonyl-3-carboxyphenoxy, 2-methanesulfonyl-4-acetylsulfamoylphenoxy, etc.), acyloxy group (acetoxyl, benzoyloxy, etc.), sulfonyloxy group (methanesulfonyloxy, benzenesulfonyloxy, etc.), acylamino group (heptafluorobutyrylamino, etc.), sulfonamide group (methanesulfonamide, etc.), alkoxycarbonyloxy group (ethoxycarbonyloxy, etc.), carbamoyloxy group (diethylcarbamoyloxy, piperidinocarbonyloxy, morpholinocarbonyloxy, etc.), alkylthio group (2-carboxyethylthio, etc.), arylthio group (2-octyloxy-5-t-octylphenylthio, 2-(2,4-di-t-amylphenoxy)butyrylamino-phenylthio, etc.), heterocyclic thio group (1-phenyltetrazolylthio, 2-benzimidazolylthio, etc.), heterocyclic oxy group (2-pyridyloxy, 5-nitro-2-pyridyloxy, etc.), 5- or 6-membered, nitrogen-containing heterocyclic group (1-triazolyl, 1-imidazolyl, 1-pyrazolyl, 5-chloro-1-tetrazolyl, 1-benzotriazolyl, 2-phenylcarbamoyl-1-imidazolyl, 5,5-dimethylhydantoin-3-yl, 1-benzylhydantoin-3-yl, 5,5-dimethylloxazolidine-2,4-

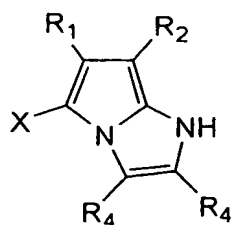
dione-3-yl, purine, etc.), azo group (4-methoxyphenylazo, 4-pivaloylaminophenylazo, etc.), etc.

The substituent represented by X is preferably an alkyl group, alkoxycarbonyl group, carbamoyl group, halogen atom, alkoxy group, aryloxy group, alkylthio group, arylthio group, or a 5- or 6-membered, nitrogen-containing heterocyclic group which bonds to the coupling active position with a nitrogen atom, and more preferably an alkyl group, carbamoyl group, halogen atom, substituted aryloxy group, substituted arylthio group, alkylthio group, or 1-pyrazolyl group. X more preferably represents a substituent.

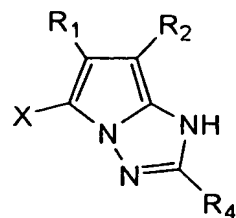
The compound preferably used in the present invention which is represented by general formulae (M-1) and (M-2) may form a polymer which is greater than or equal to a dimer through  $R_{11}$  and  $R_{12}$ , or may bond to a macromolecular chain. In the present invention, formula (M-1) is preferable and formula (M-3) is more preferable.

Next, general formula (C) will be described. The formula (C) of the present invention is specifically expressed by the following formulae (C3) to (C10):

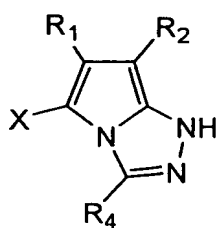




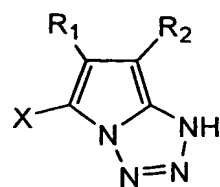
(C3)



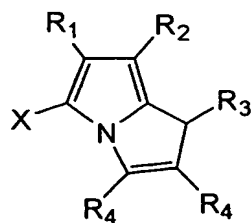
(C4)



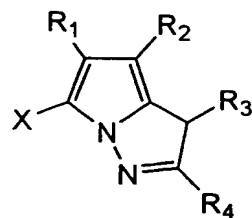
(C5)



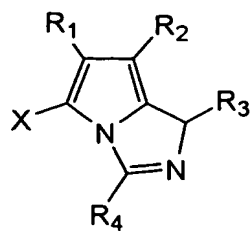
(C6)



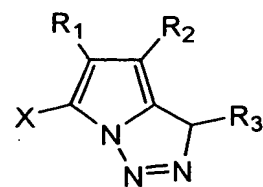
(C7)



(C8)



(C9)



(C10)

In the formulae,  $R_1$  to  $R_4$  and  $X$  have the same meanings as those defined in formula (C).

In the present invention, the compounds

represented by formulae (C3), (C4), (C5) and (C8) are preferable, and the compound represented by (C4) is especially preferable.

5 In formula (C), the substituent represented by  $R_1$ ,  $R_2$  and  $R_3$  is an electron attractive group having a Hammett constant  $\sigma_p$  value of 0.20 to 1.0, preferably an electron attractive group having a  $\sigma_p$  value of 0.20 to 0.8. Hammett's rule is an empirical rule proposed by L. P. Hammett in 1935 in order to quantitatively argue the effects of substituents on reaction or equilibrium of benzene derivatives. The rule is widely regarded as appropriate these days. The substituent constants obtained by the Hammett rule include a  $\sigma_p$  value and a  $\sigma_m$  value, and these values are described in a large amount of general literature. For example, the values are described in detail in J. A. Dean ed., "Lange's Handbook of Chemistry," the 12th edition, 1979 (McGraw-Hill), "The Extra Number of The Domain of Chemistry (KAGAKUNO RYOIKI ZOUKAN)," Vol. 122, pages 96 to 103, 15 1979 (Nanko Do) and Chemical Reviews, Vol. 91, pp. 165-195 (1991).

25 In the present invention,  $R_1$ ,  $R_2$ , and  $R_3$  are defined by the Hammett constant  $\sigma_p$  value. However, this does not mean that  $R_1$ ,  $R_2$ , and  $R_3$  are limited to substituents having the known values stated in the above literature. That is, the present invention includes, of course, substituents having values that

fall within the above range when measured on the basis of Hammett's rule even if they are unknown in literature.

5        Examples of  $R_1$ ,  $R_2$ , and  $R_3$ , as the electron attractive group having a  $\sigma_p$  value of 0.2 to 1.0, are an acyl group, alkoxycarbonyl group, aryloxy carbonyl group, carbamoyl group, cyano group, nitro group, dialkylphosphono group, diarylphosphono group, diarylphosphinyl group, alkylsulfinyl group,  
10        arylsulfinyl group, alkylsulfonyl group, arylsulfonyl group, etc. Of these substituents, those capable of further having substituents can further have substituents to be enumerated later for  $R_4$ .

15         $R_1$ ,  $R_2$ , and  $R_3$  preferably represent an acyl group, alkoxycarbonyl group, aryloxy carbonyl group, carbamoyl group, cyano group, and sulfonyl group, and more preferably, an cyano group, acyl group, alkoxycarbonyl group, aryloxy carbonyl group, and carbamoyl group.

20        A preferable example of the combination of  $R_1$  and  $R_2$ , is one wherein  $R_1$  represents a cyano group and  $R_2$  represents an alkoxycarbonyl group.

$R_4$  represents a hydrogen atom or substituent. Examples of the substituent are those enumerated above for  $R_{11}$ .  $R_4$  preferably represents a substituent.

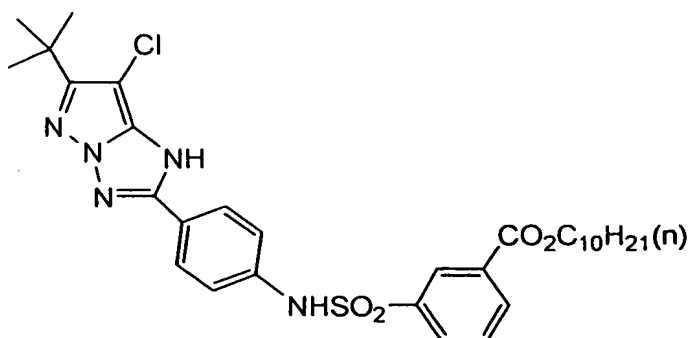
25        Preferable examples of the substituents represented by  $R_4$  are an alkyl group, aryl group, heterocyclic group, alkoxy group, aryloxy group, and

acylamino group. An alkyl group and substituted aryl group are more preferable, and a substituted aryl group is most preferable. Examples of the substituent in this case are those enumerated above for  $R_4$ .

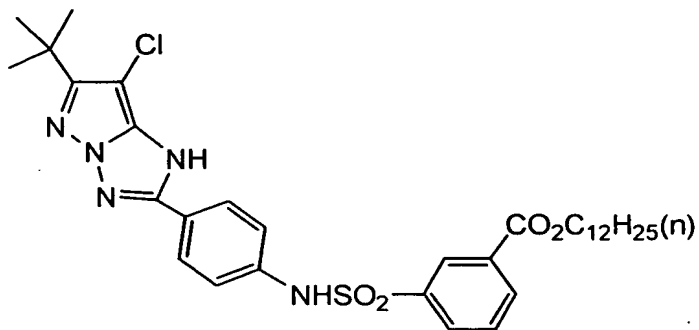
- 5           X has the same meaning as that defined in formula (M).

          The following are examples of a coupler preferably used in the present invention. However, the present invention is not limited to these examples.

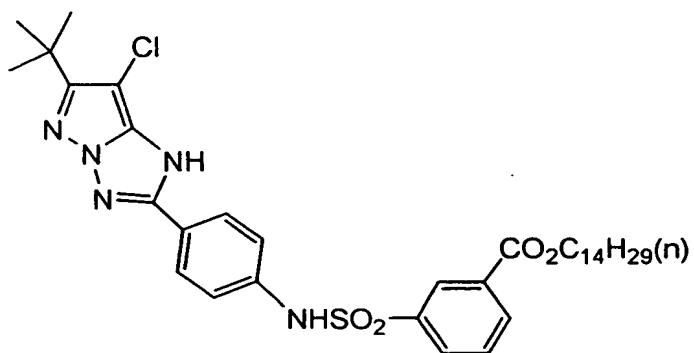
(1)



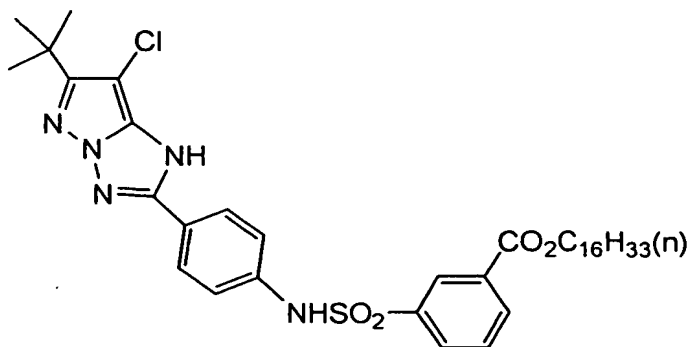
(2)

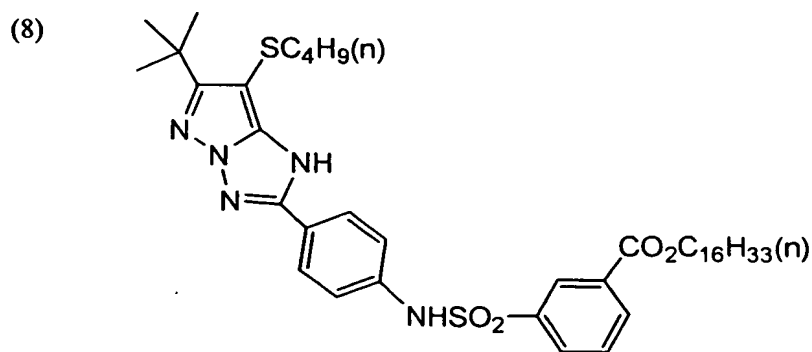
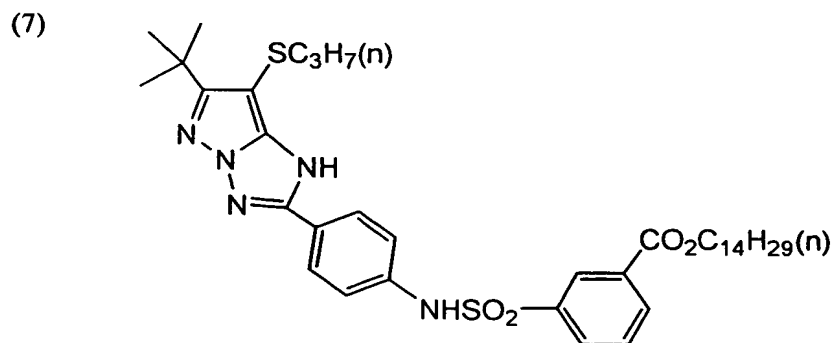
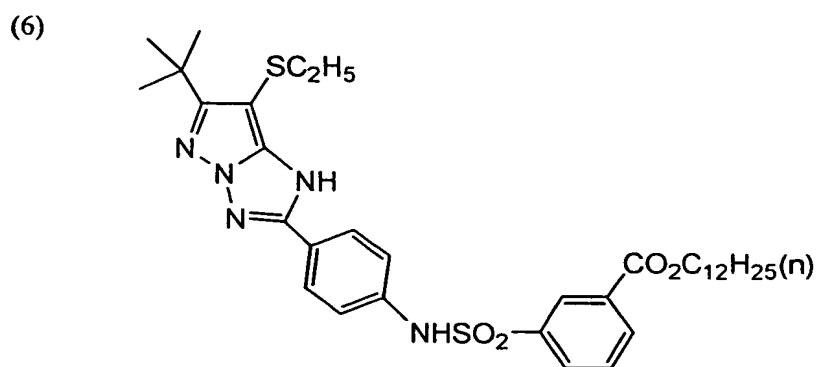
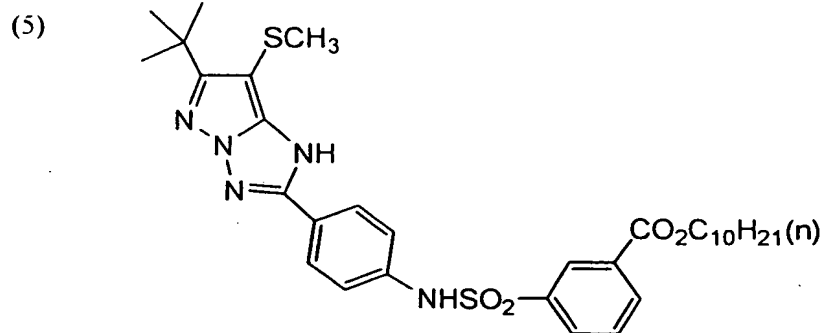


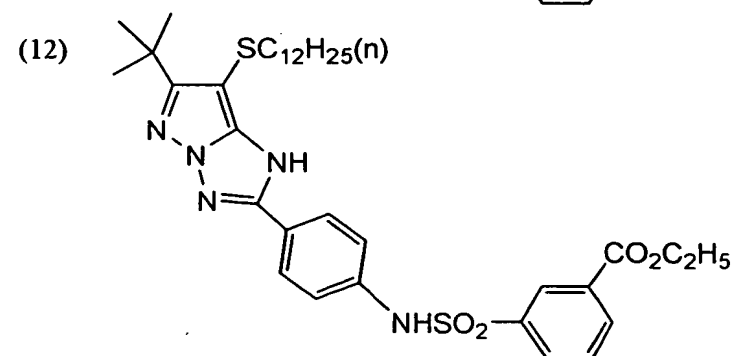
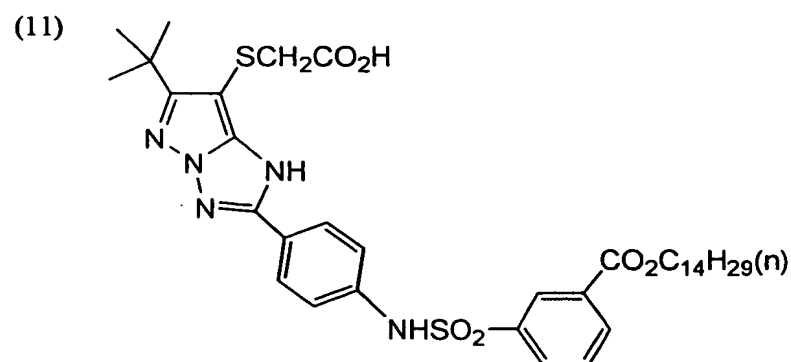
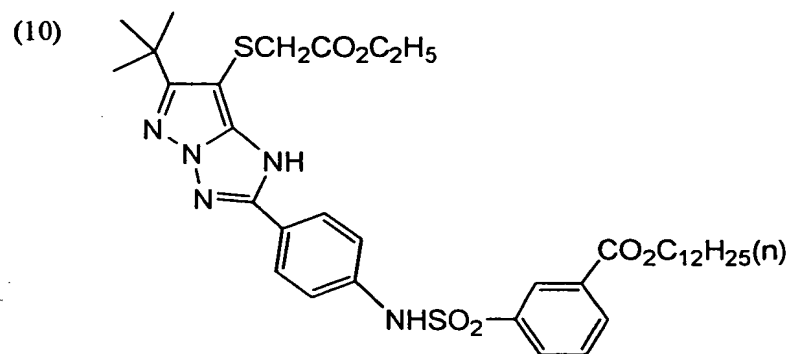
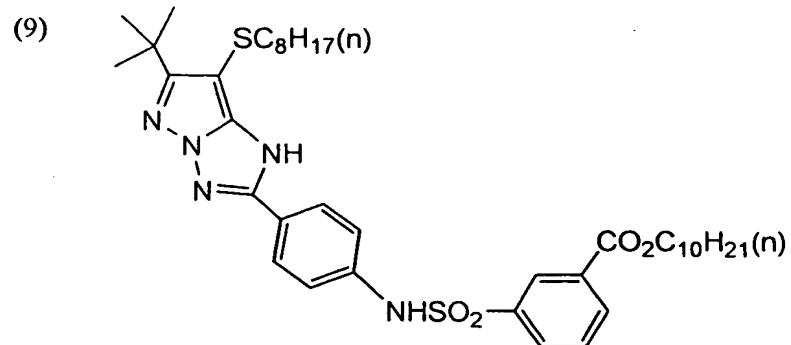
(3)

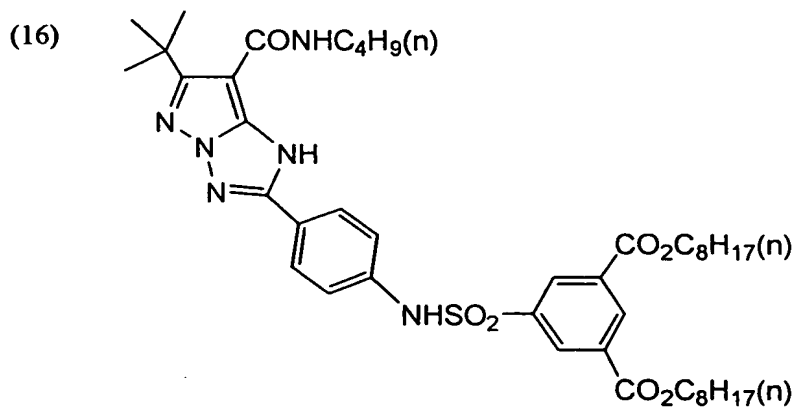
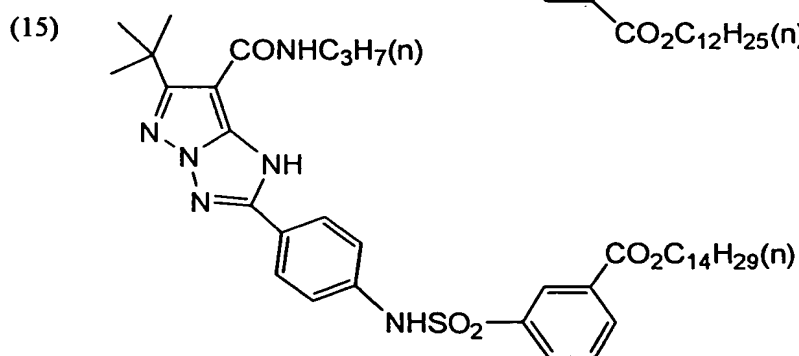
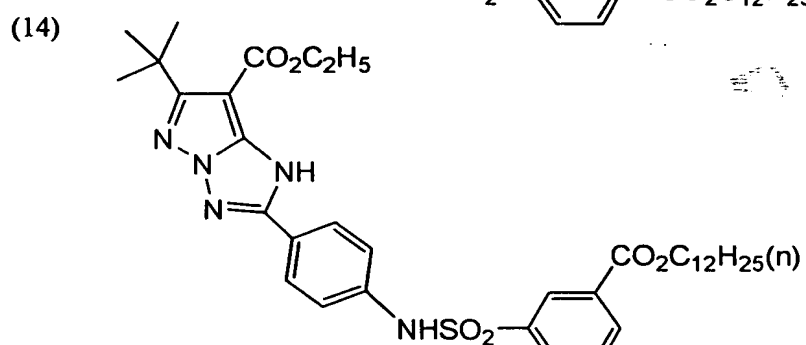
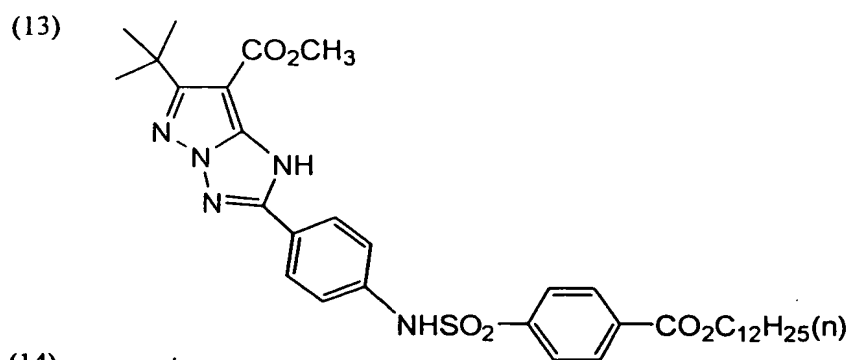


(4)

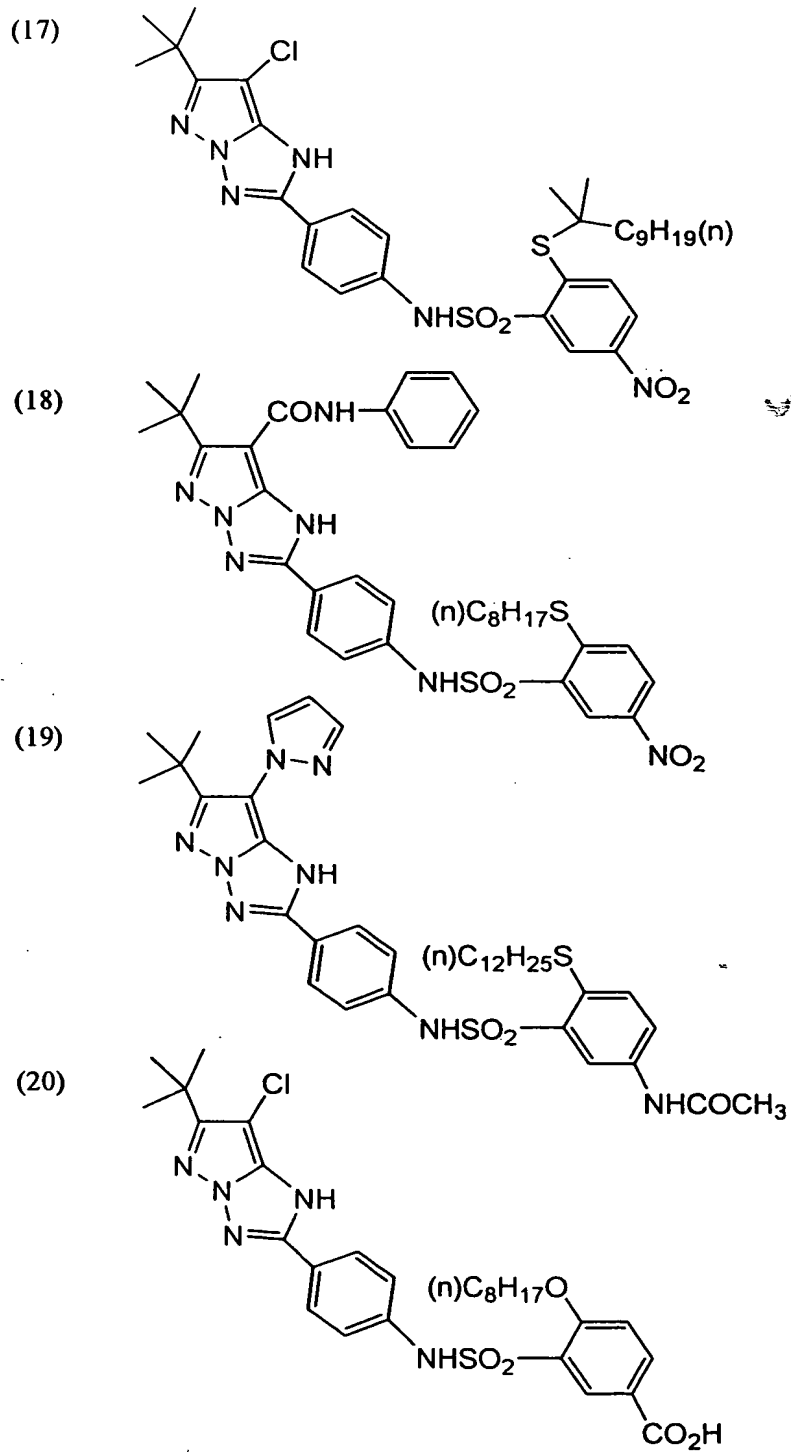


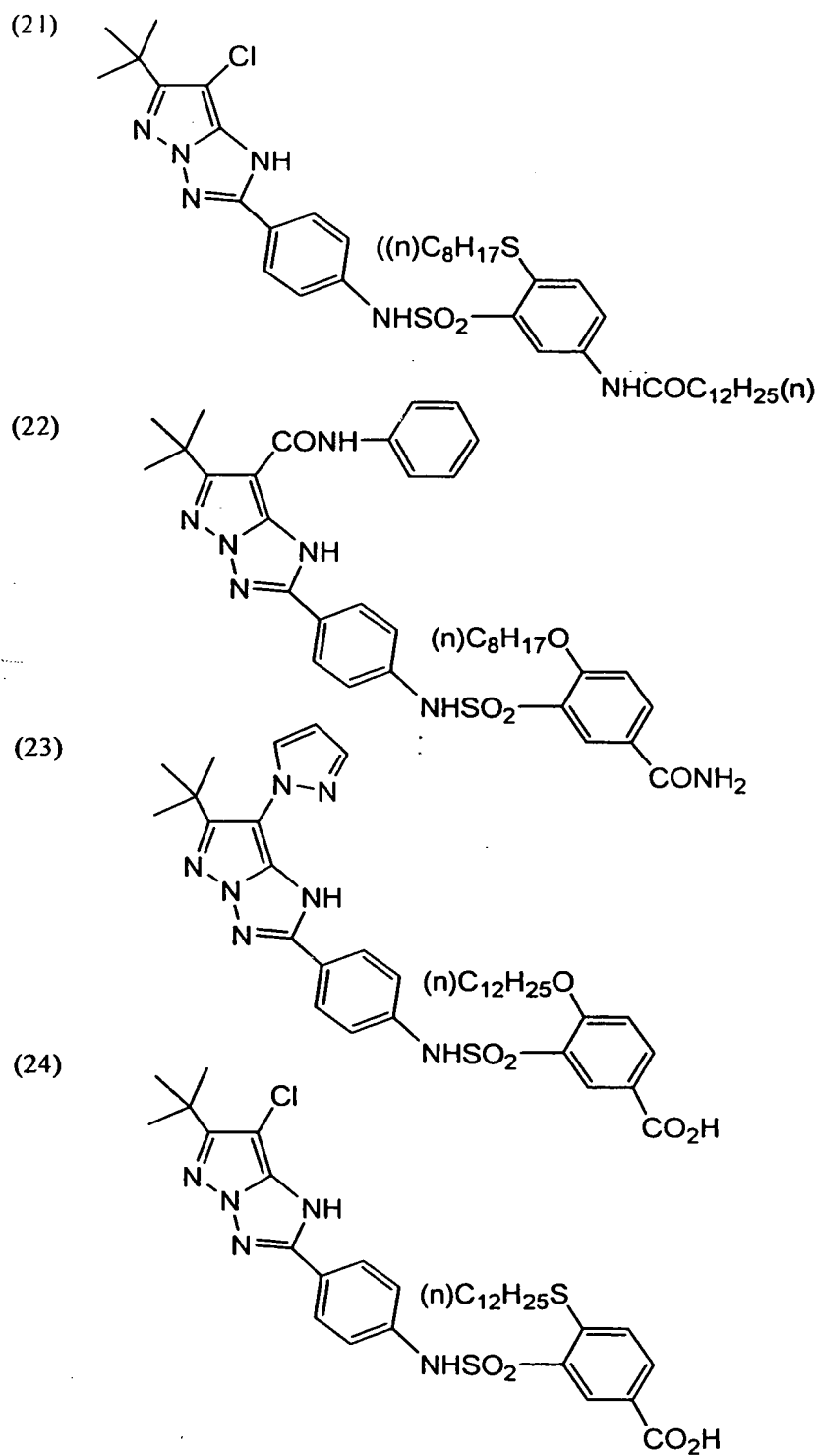


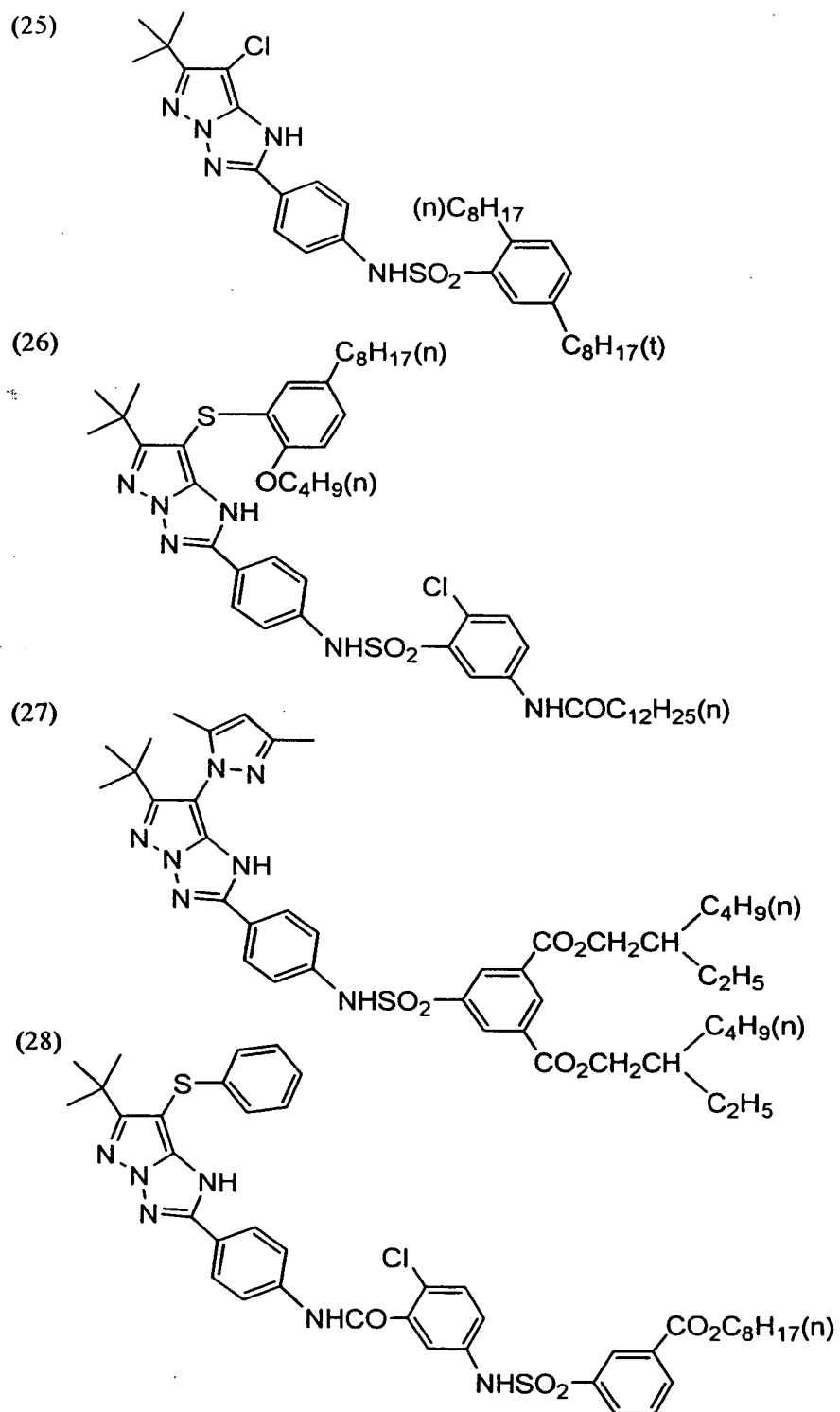




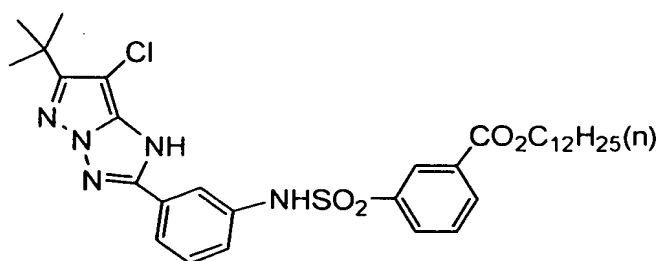




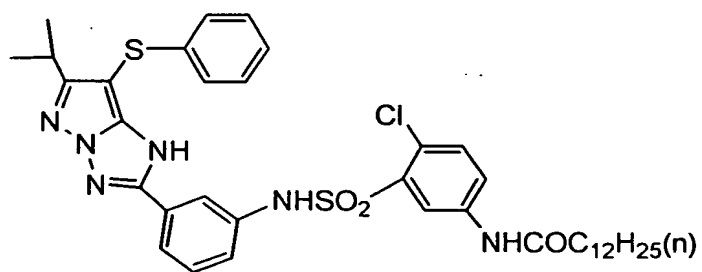




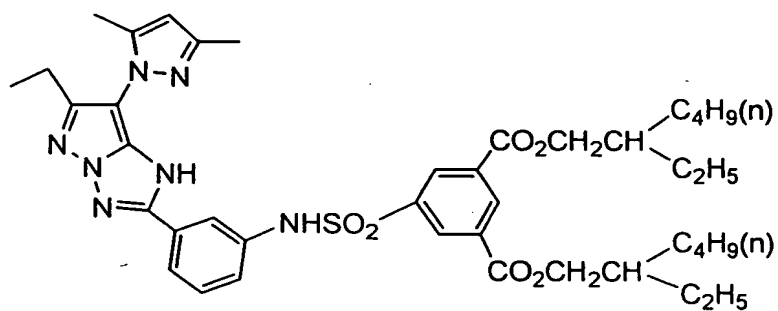
(29)



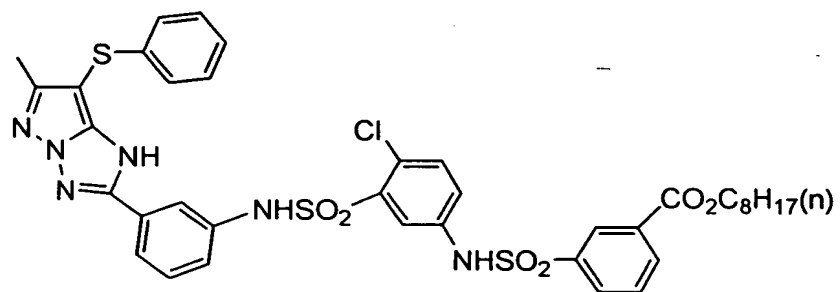
(30)



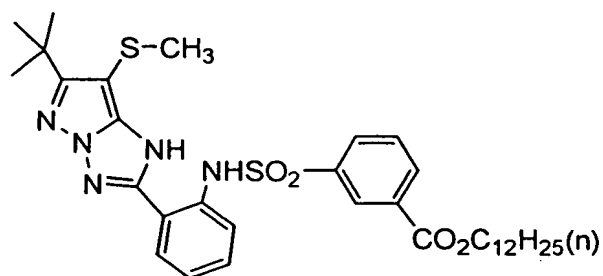
(31)



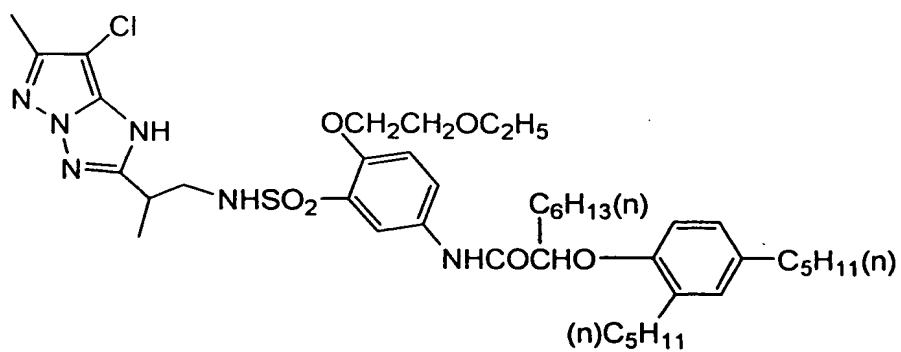
(32)



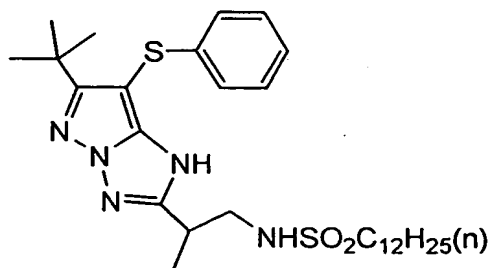
(33)



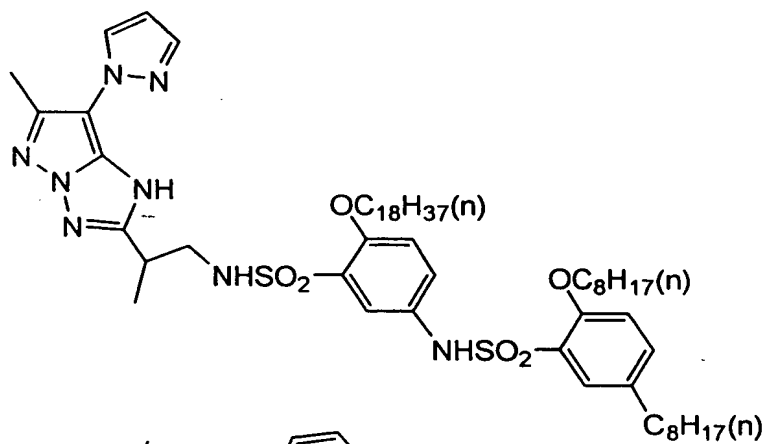
(34)



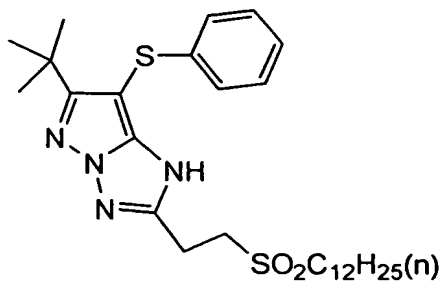
(35)



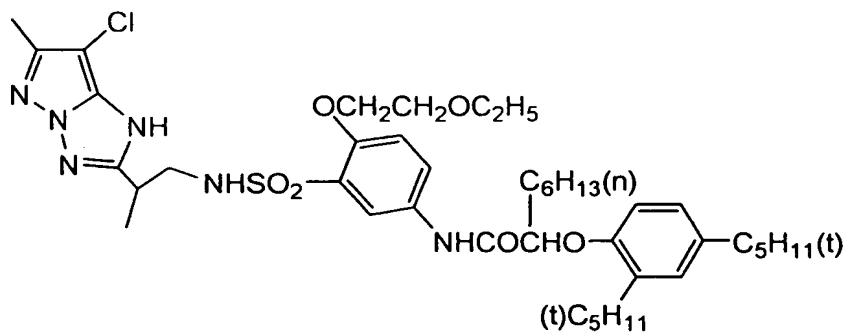
(36)



(37)

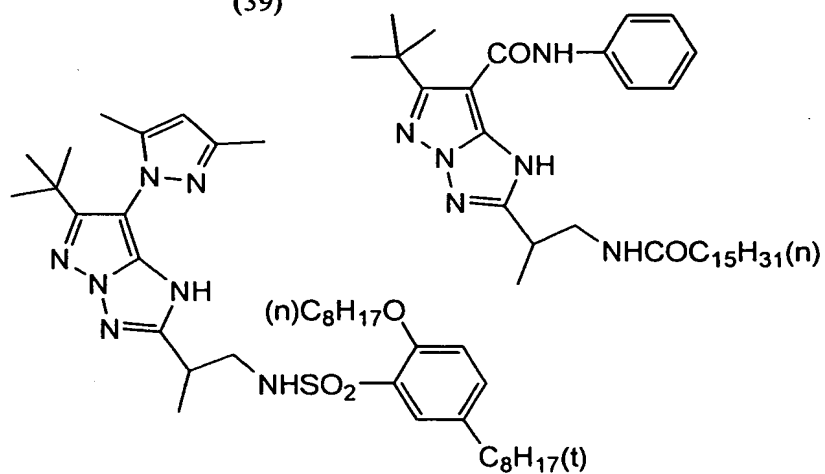


(38)



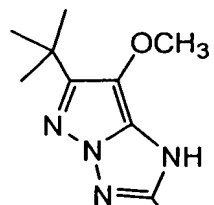
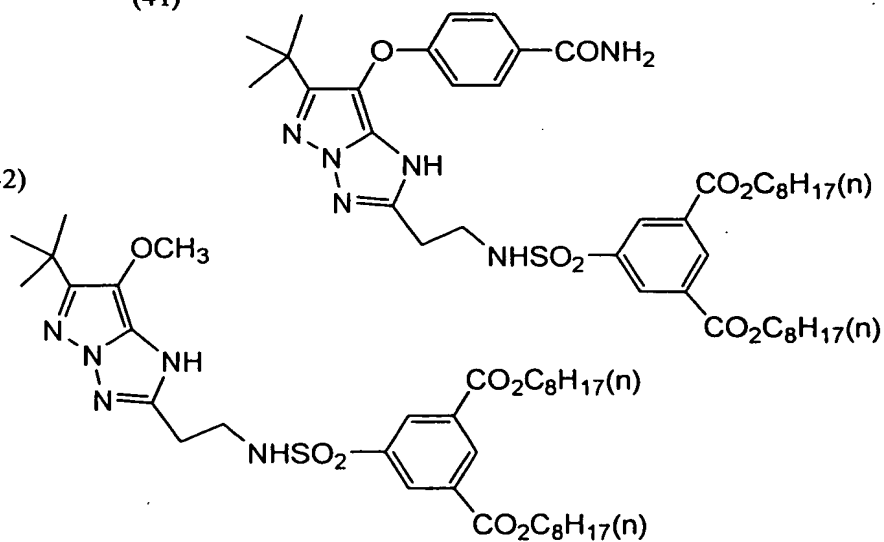
(39)

(40)

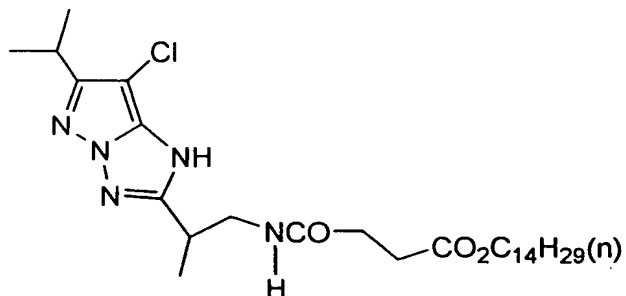


(41)

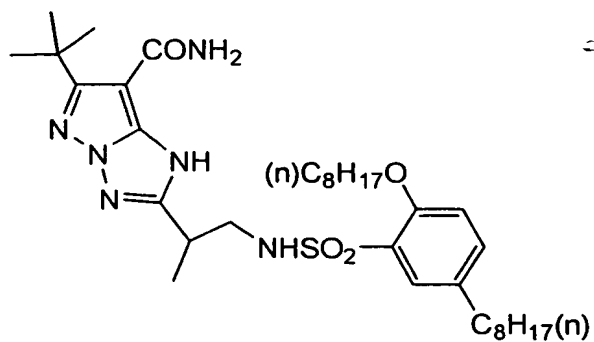
(42)



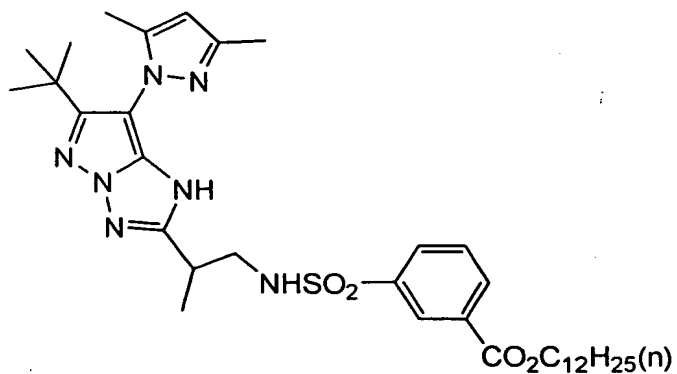
(43)



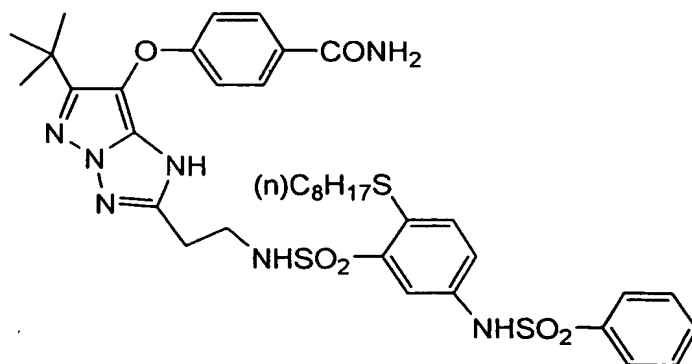
(44)



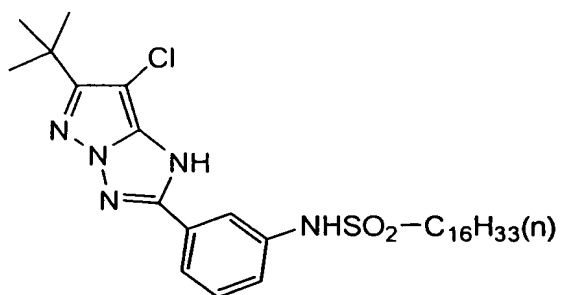
(45)



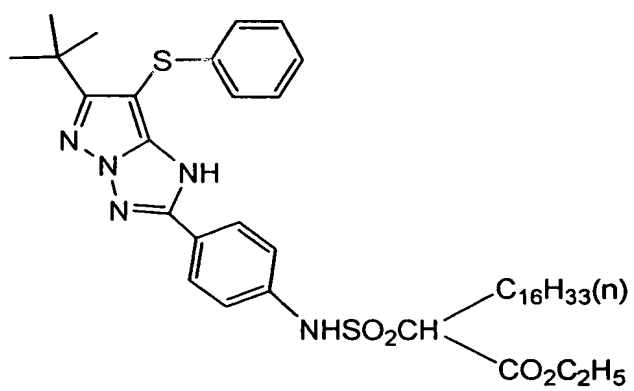
(46)



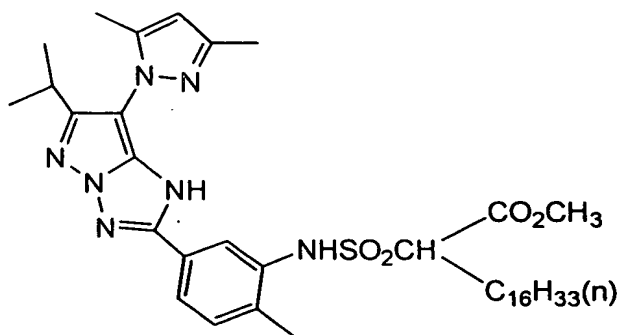
(47)



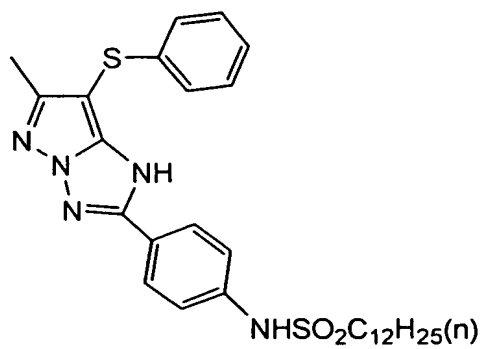
(48)



(49)

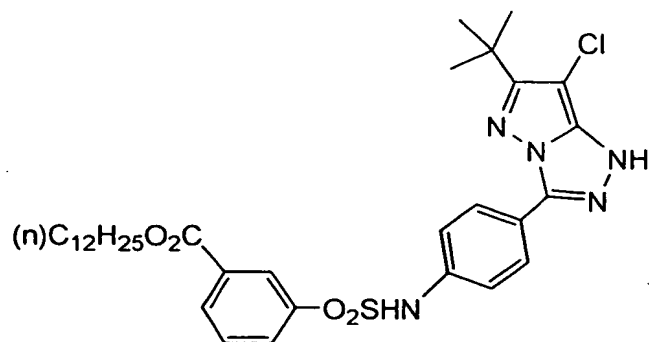


(50)

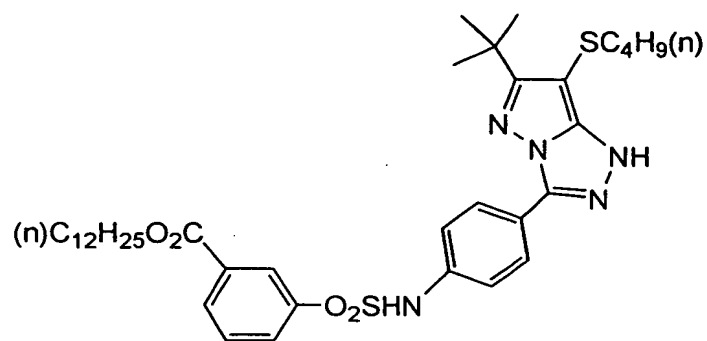




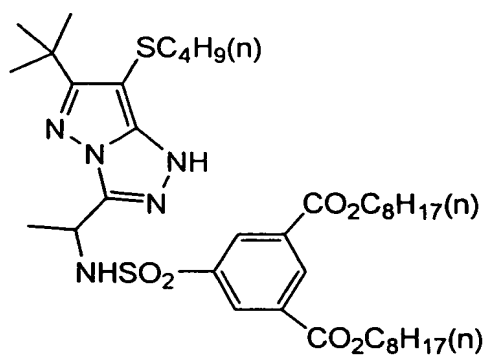
(51)



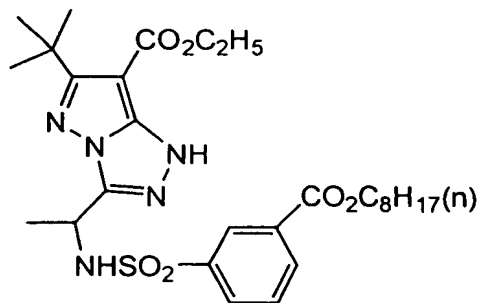
(52)

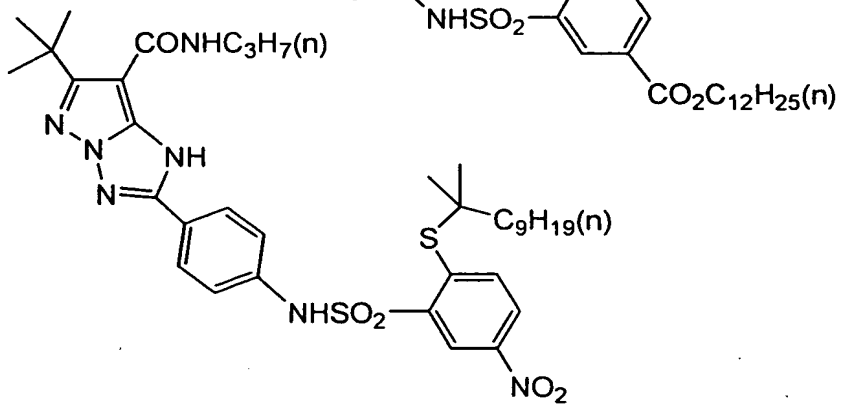
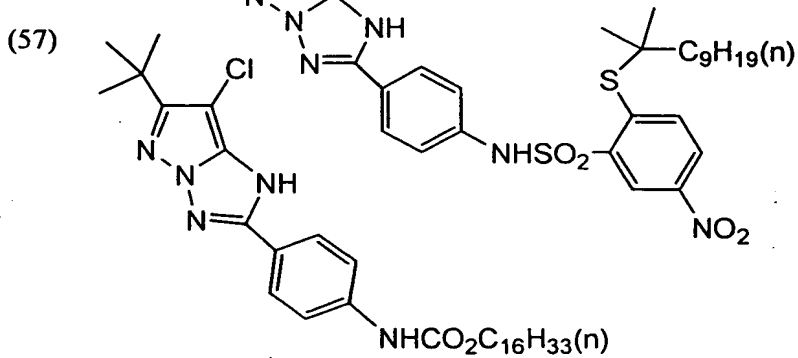
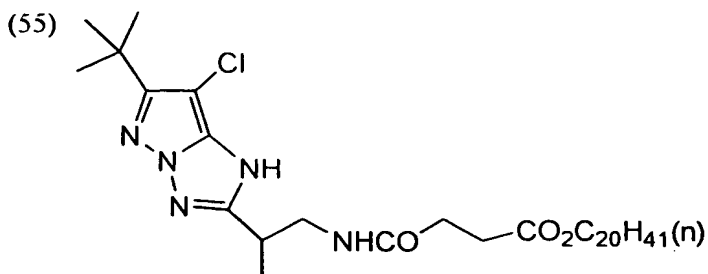


(53)

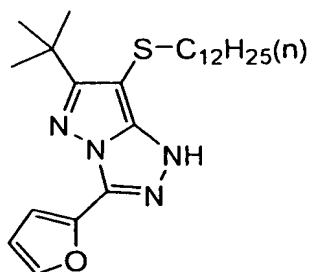


(54)

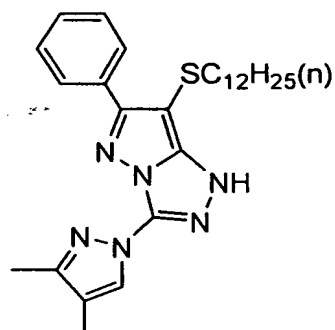




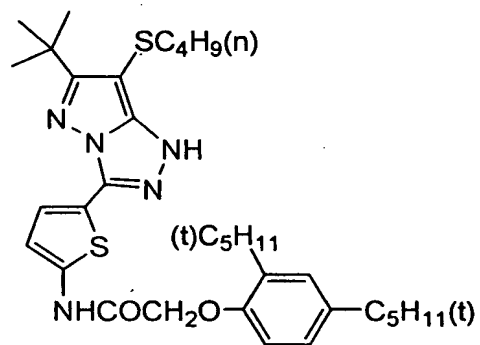
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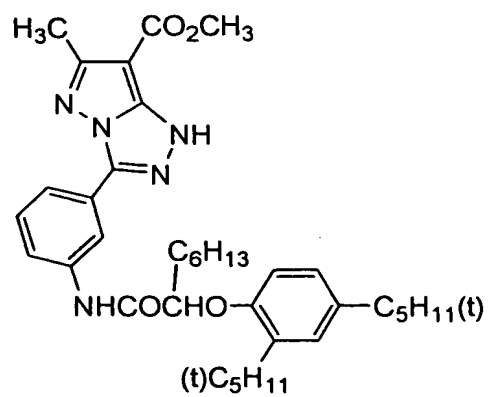
(61)

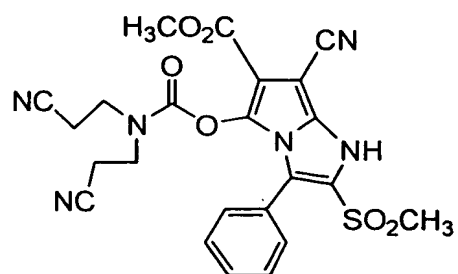
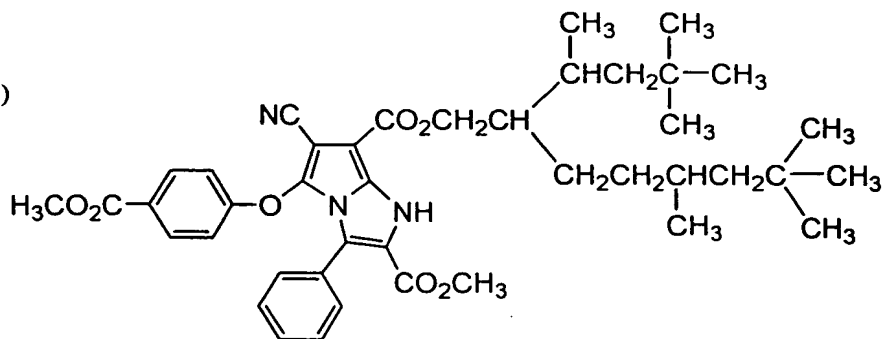
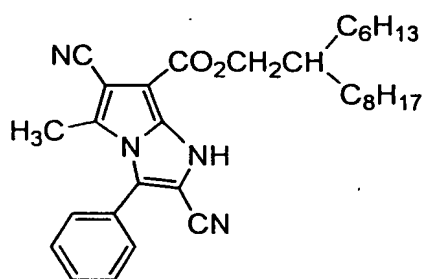
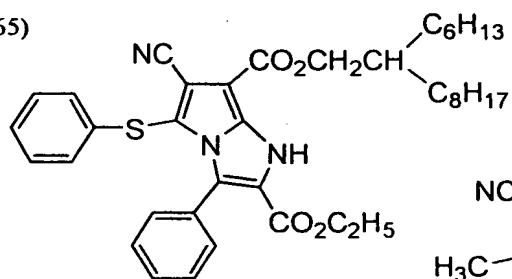
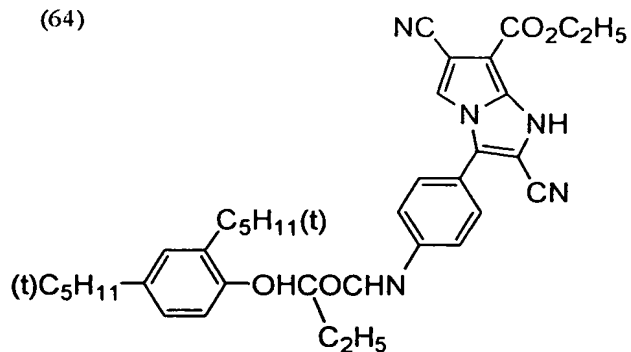


(62)

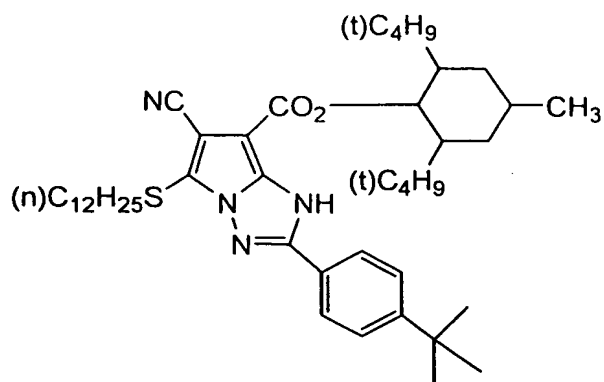


(63)

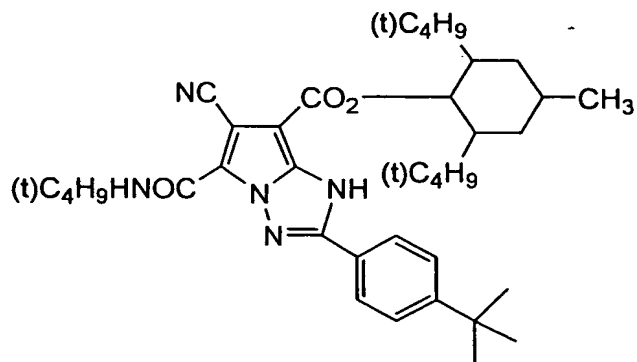




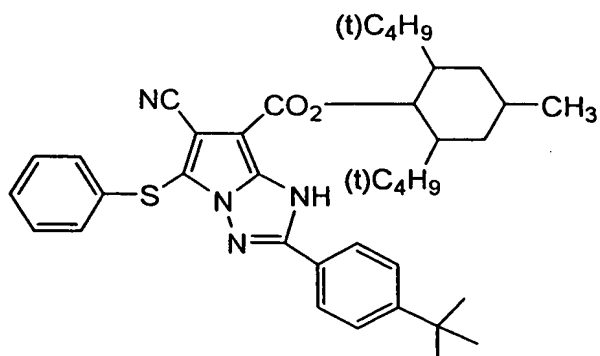
(69)



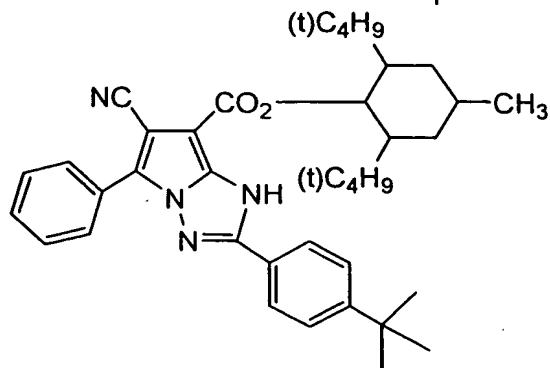
(70)



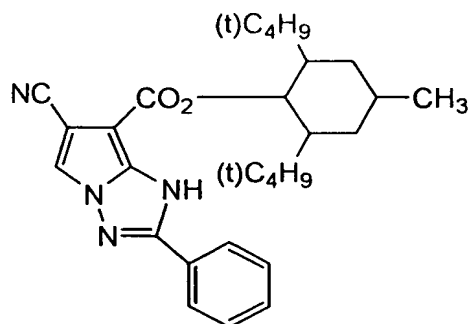
(71)



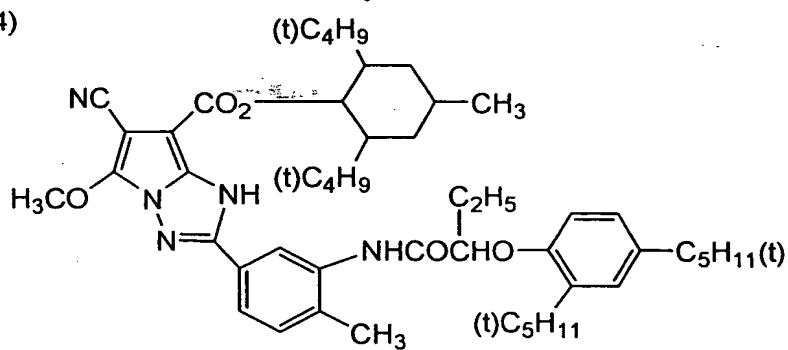
(72)



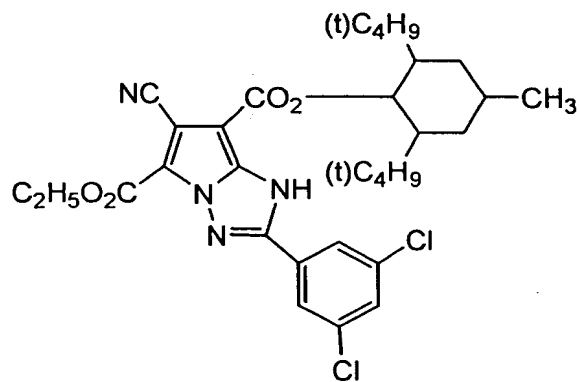
(73)



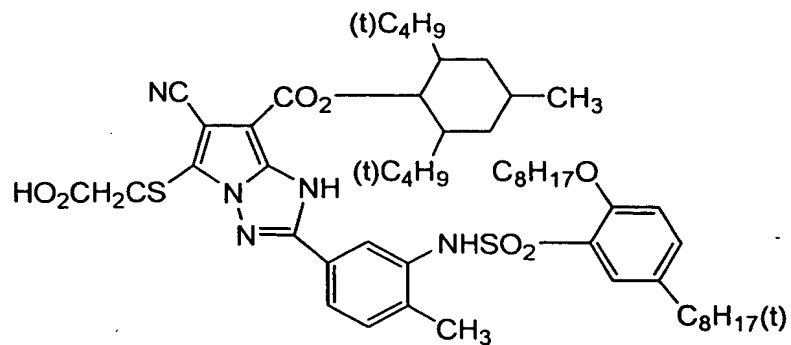
(74)



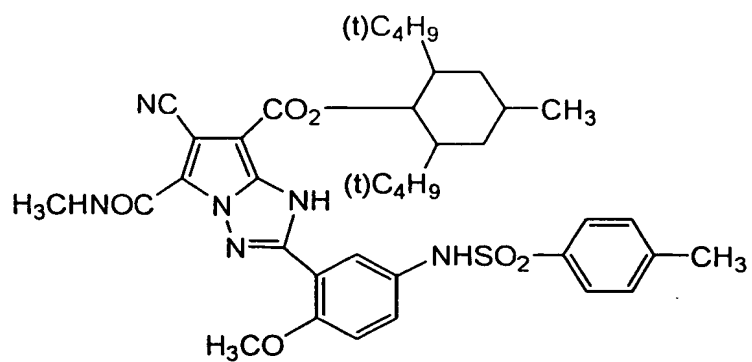
(75)



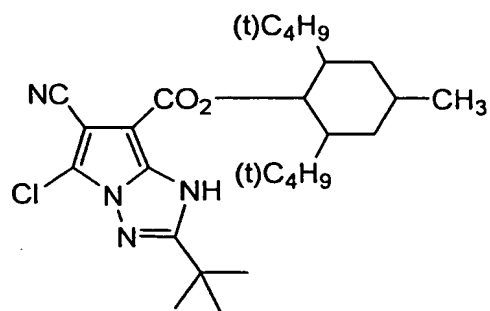
(76)



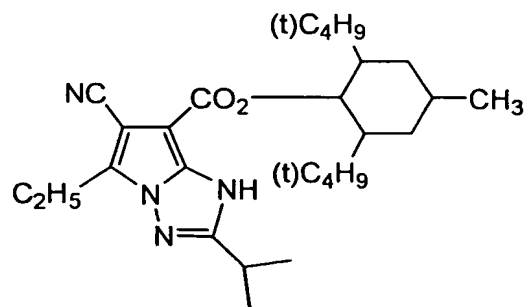
(77)



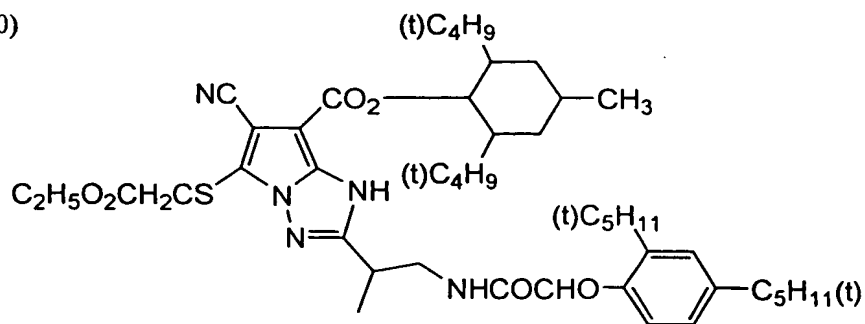
(78)



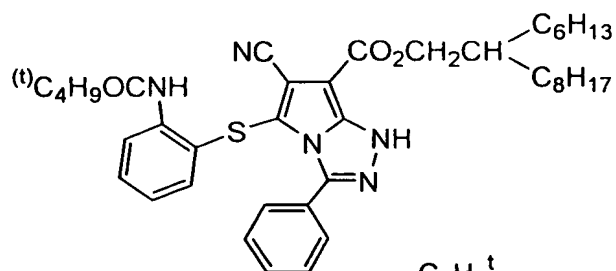
(79)



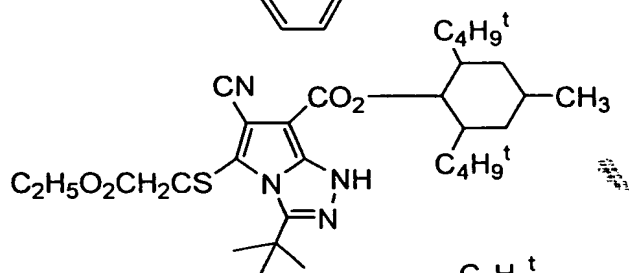
(80)



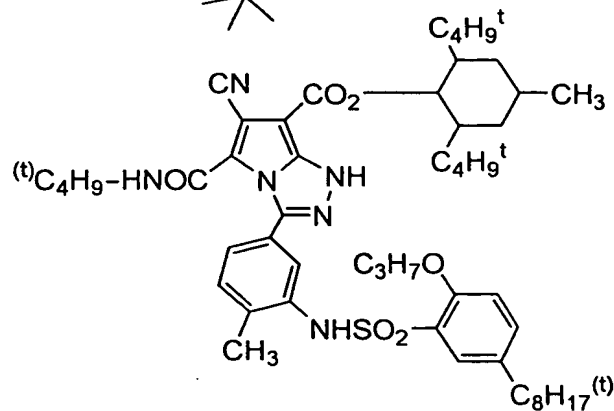
(81)



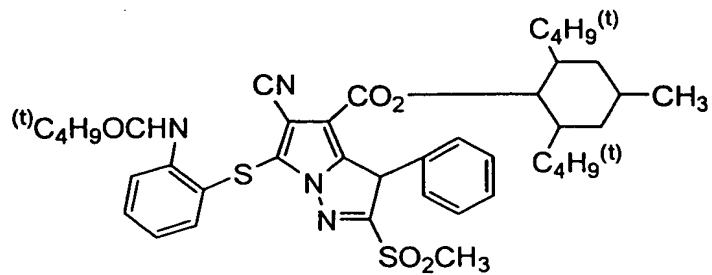
(82)



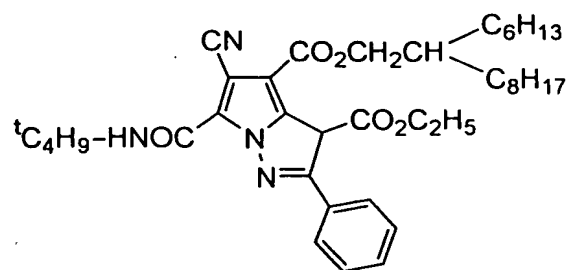
(83)



(84)

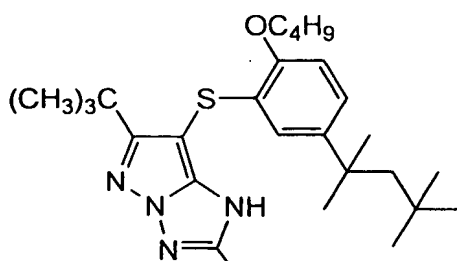


(85)

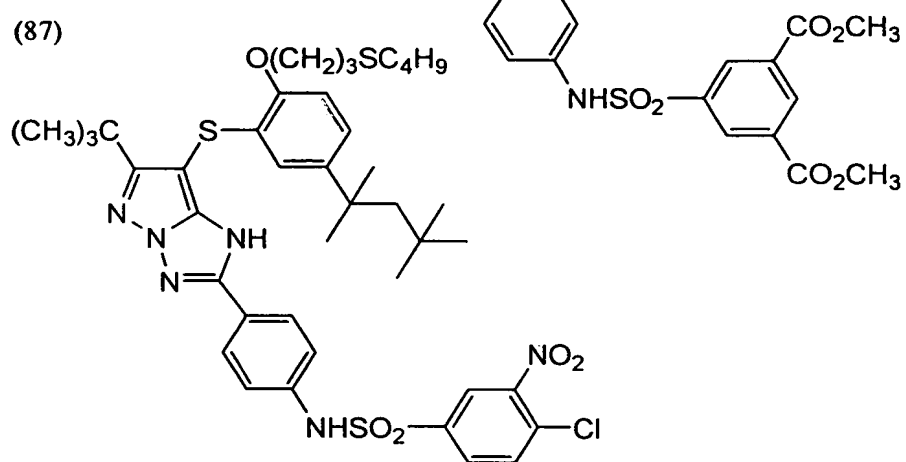




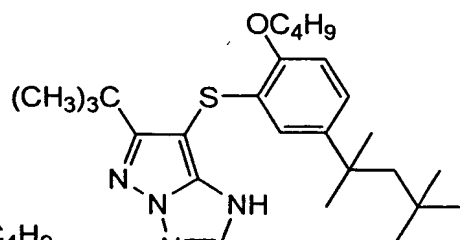
(86)



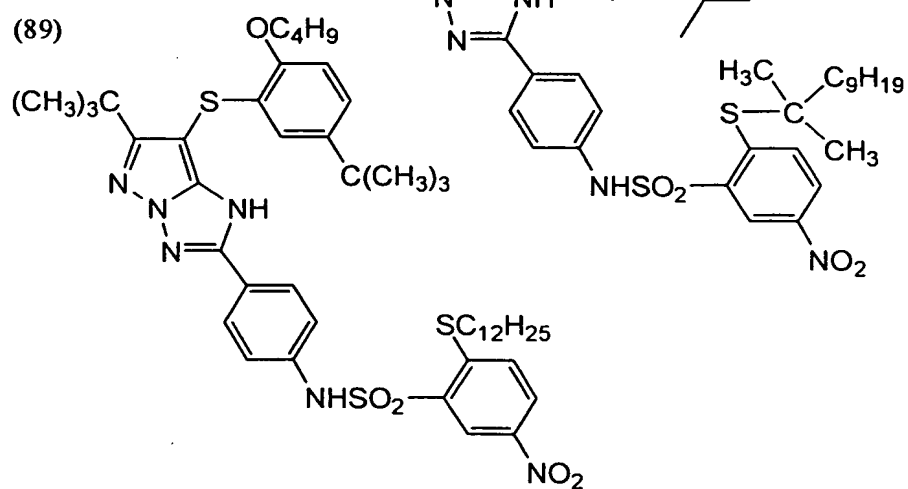
(87)

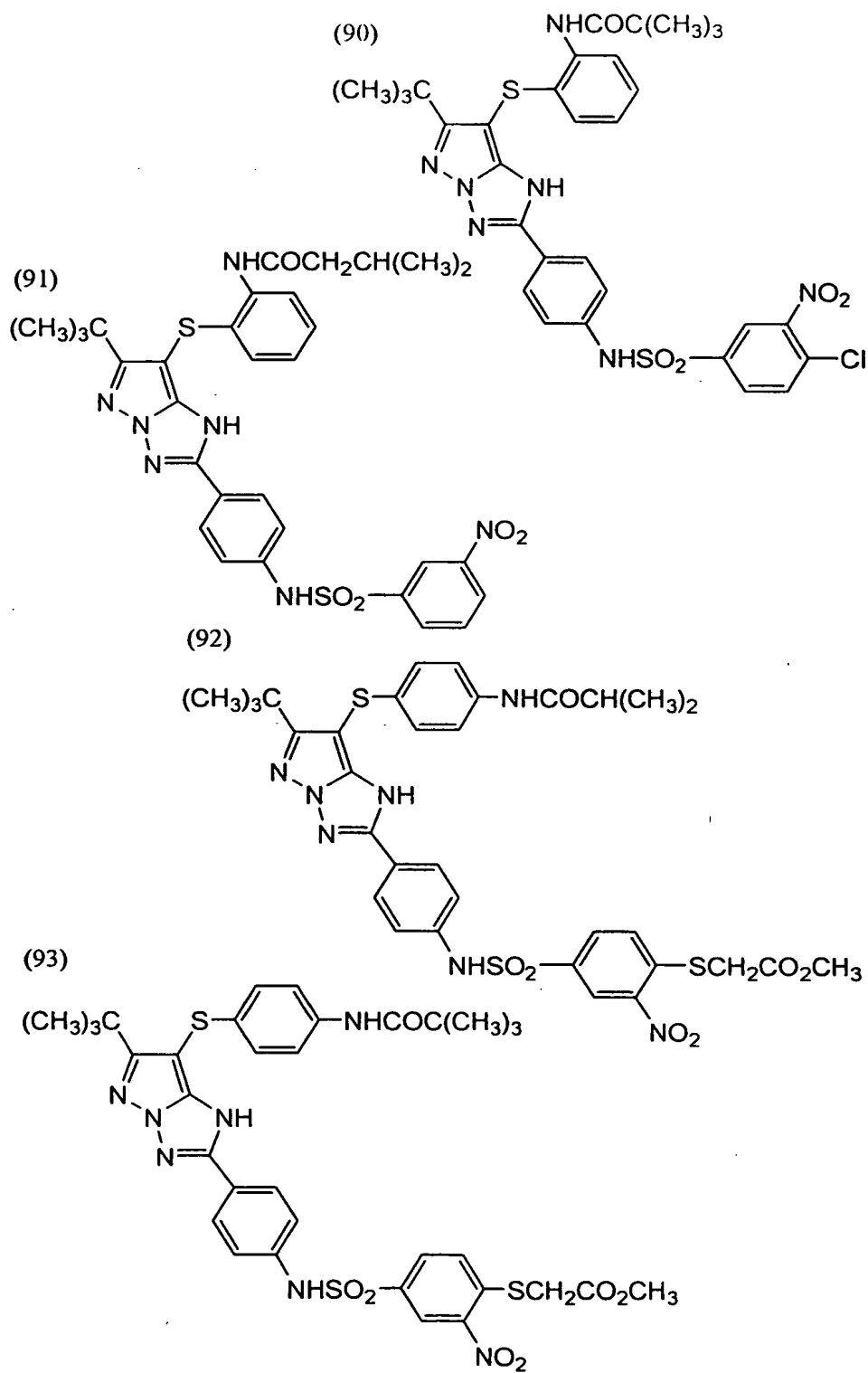


(88)

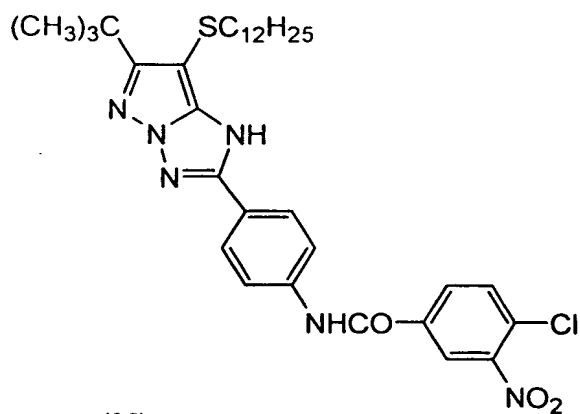


(89)

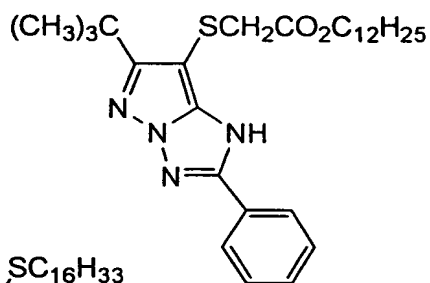




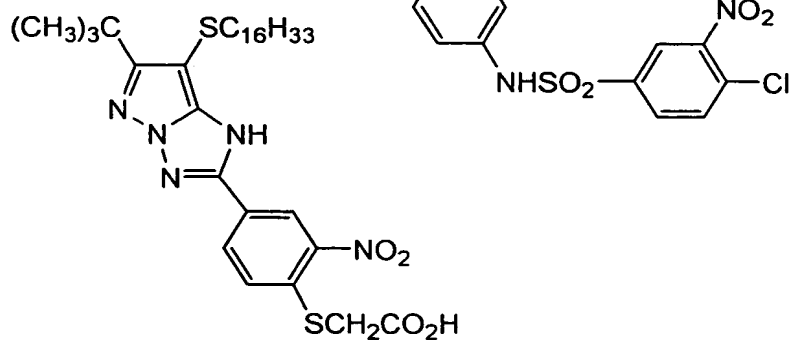
(94)



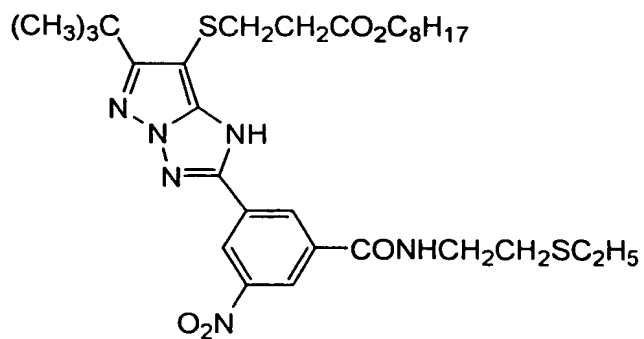
(95)

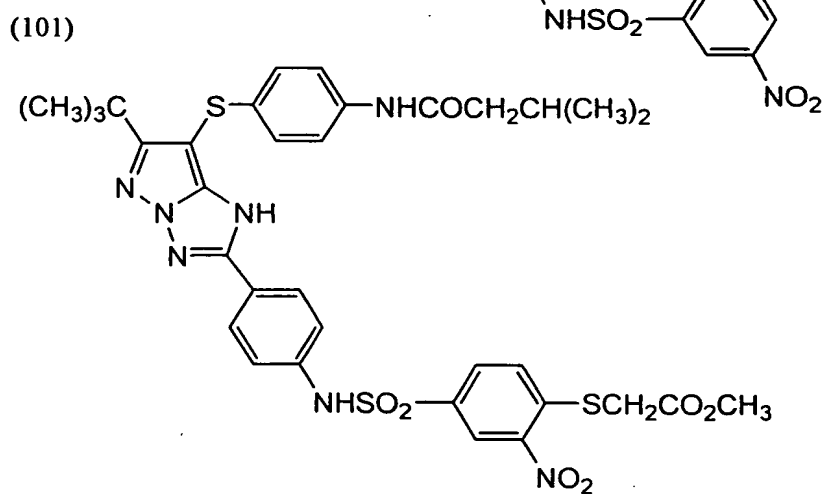
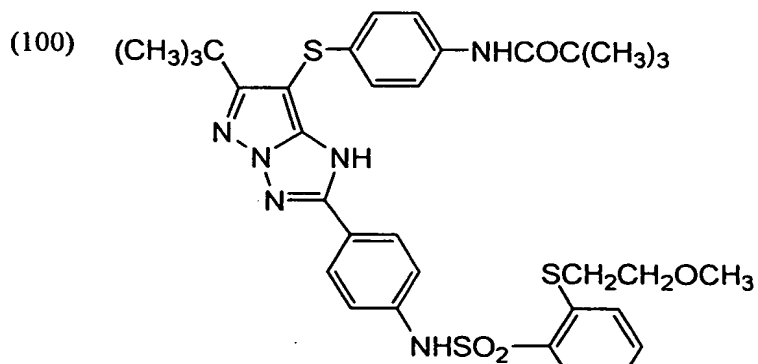
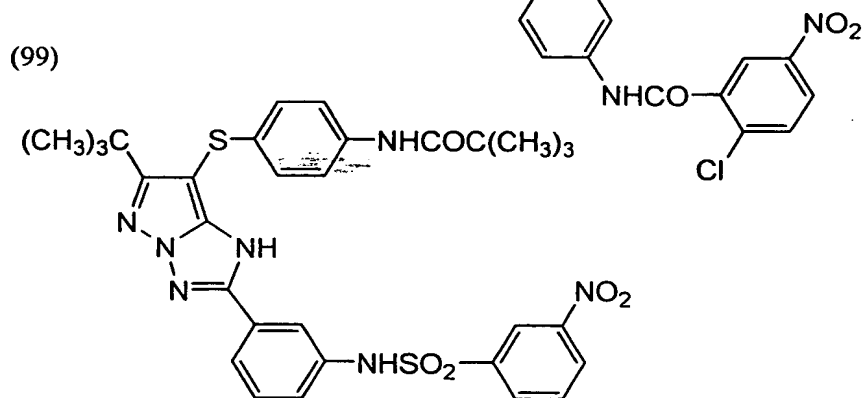
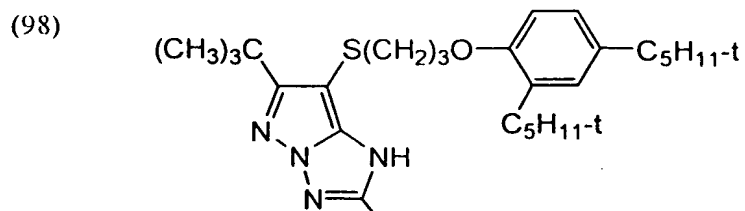


(96)

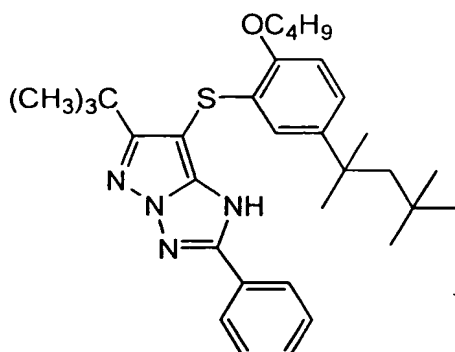


(97)

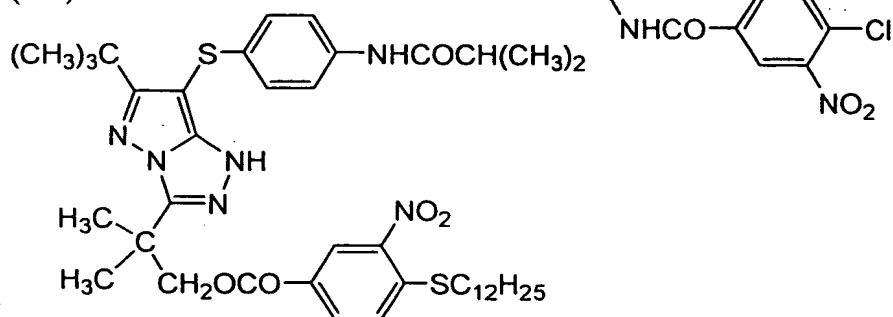




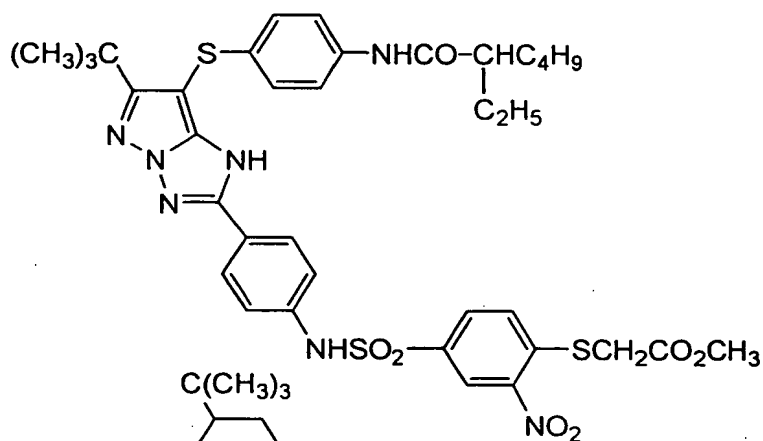
(102)



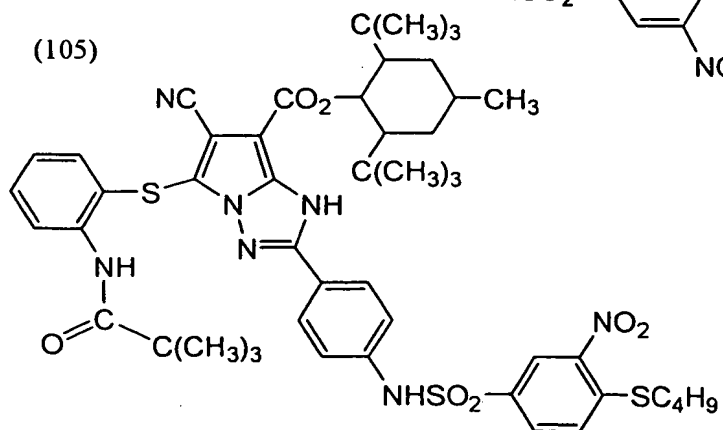
(103)



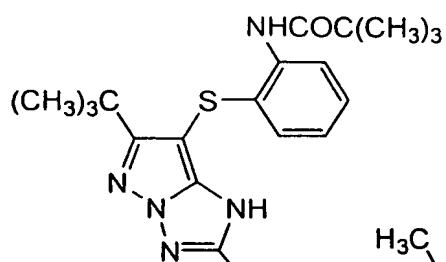
(104)



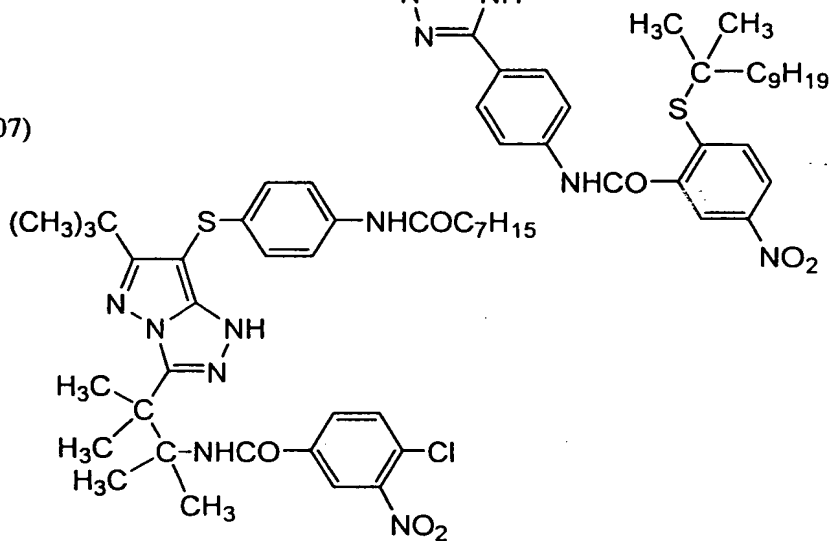
(105)



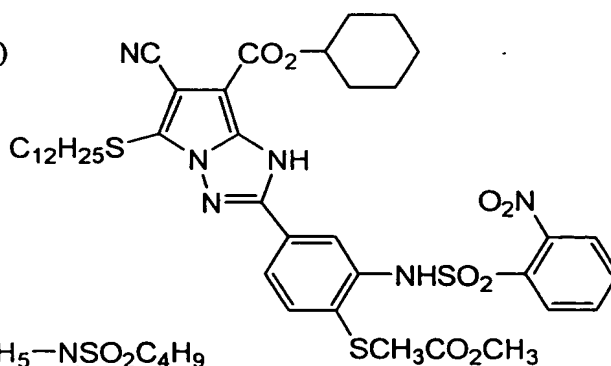
(106)



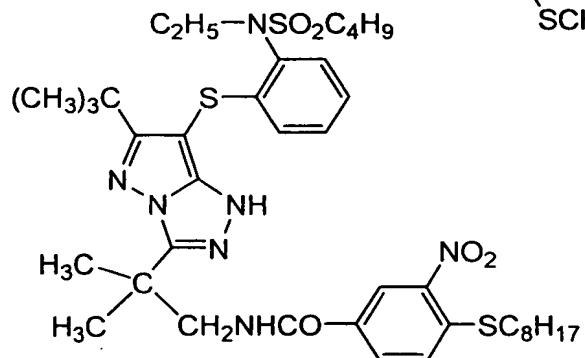
(107)



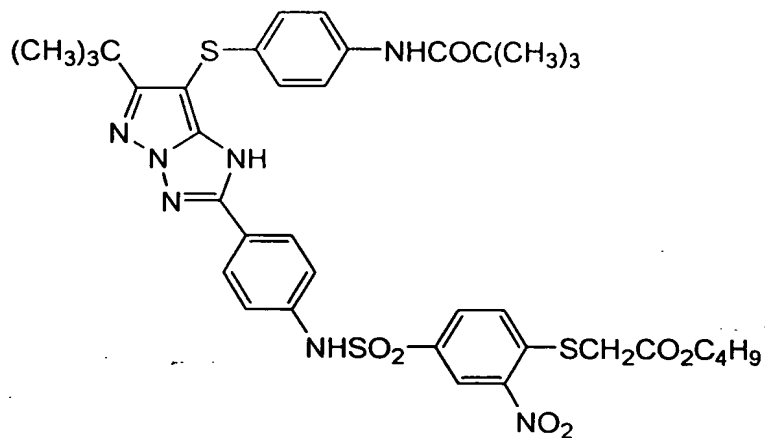
(108)



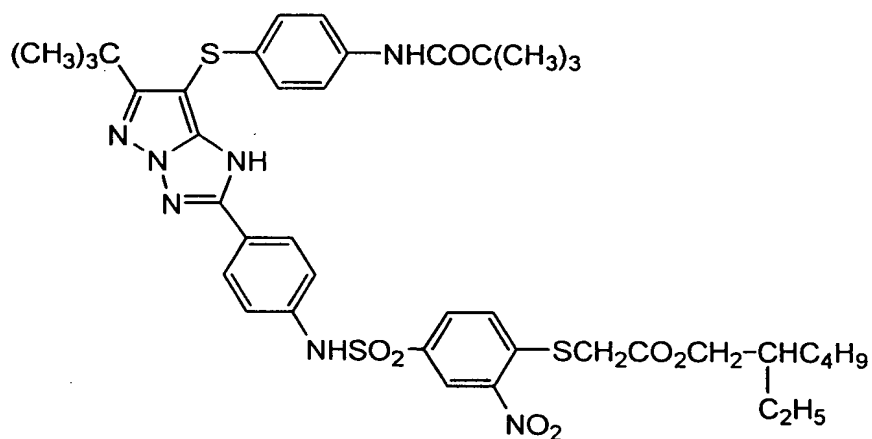
(109)



(110)



(111)



The compound of the present invention can easily be prepared according to the synthesis methods described in JP-A's-61-65245, 61-65246, 61-147254 and 8-122984, etc.

In the present invention, the addition location and so on of the compound represented by general formula (M) or (C) is not limited as long as the compound is able to act on the silver halide color photographic material. However, the compound is preferably contained in the silver halide color photographic material. When the compound represented

by general formula (M) or (C) of the present invention is contained in the silver halide color photographic material, the compound may be used in any of the silver halide light-sensitive layer and nonsensitive layer.

5 It is also preferable that the compound represented by general formula (M) or (C) of the present invention is added to both a light-sensitive layer and nonsensitive layer.

10 If the compound of the present invention is used in the silver halide light-sensitive layer, and the light-sensitive layer is divided into a plurality of layers of different speeds, the compound can be used for the layer of any speed. However, it is preferable that the compound be used for the highest speed layer.

15 If the compound is used in the nonsensitive layer, it is preferable that the compound be used for the nonsensitive layer disposed between the red-sensitive layer and the green-sensitive layer, or between the green-sensitive layer and the blue-sensitive layer.

20 The nonsensitive layer refers to all the layers other than the silver halide emulsion layer. Examples of the nonsensitive layers are an antihalation layer, an interlayer, a yellow filter layer, and a protective layer.

25 The method and the time of adding the compound of general formula (M) or (C) to the photosensitive material is not particularly limited. There are the



methods as follows: a method of emulsifying and dispersing the compound with a high boiling organic solvent; solid-state dispersion; a method of dissolving the compound in an organic solvent such as methanol and adding the obtained product to a coating liquid; and a method of adding the compound at the time of preparing the silver halide emulsion. It is preferable, however, that the compound be introduced in the photosensitive material by emulsification and dispersion.

As stated in the description of the prior art, in general, the speed depends on the grain size of a silver halide emulsion. The larger the grain size of the emulsion, the more the speed increases. However, since the graininess deteriorates with increase of the size of a silver halide grain, the speed and graininess have a trade-off relationship.

In addition to increasing the grain size of the silver halide emulsion, it is possible to increase the speed of the material by increasing the activity of a coupler, or reducing the amount of a development inhibitor releasing coupler (DIR coupler). However, if the speed is increased by these methods, the graininess deteriorates simultaneously. These methods such as change of the grain size of the emulsion, regulation of the activity of the coupler, control of the DIR coupler are mere "regulation means" for, in the trade-off relationship between the speed and graininess,

increasing the speed while deteriorating the graininess,  
or reducing the speed while improving the graininess.

"A method of increasing speed" recited in the  
claims is not the above-mentioned speed increasing  
5 method involving deterioration of the graininess  
corresponding to the speed increase.

A method of increasing speed of the present  
invention is a speed-increasing method not causing  
deterioration of the graininess, or a speed-increasing  
10 method wherein the degree of increasing the speed is  
larger compared with the degree of deterioration in the  
graininess. If the speed increase and the graininess  
deterioration occur simultaneously, it is required to  
use the above "regulation means" to match the  
15 graininess and then compare the speed, and to obtain a  
substantial speed increase.

"Substantial speed increase" means a speed  
difference between the photosensitive material with the  
compound represented by the general formula (M) or (C)  
20 and that without the compound represented by the  
general formula (M) or (C) is 0.03 or more. The speed  
of the photosensitive material is measured after  
exposing the photosensitive materials through a  
continuous wedge. The speed is defined as the  
25 logarithmic value of the reciprocal of the exposure  
amount that provides the minimum density plus 0.2.

The addition amount of the compound of general

formula (M) or (C) is preferably 0.1 to 1000 mg/m<sup>2</sup>, more preferably, 1 to 500 mg/m<sup>2</sup>, and especially preferably, 5 to 100 mg/m<sup>2</sup>.

If the compound is used for the light-sensitive silver halide emulsion layer, the amount thereof is preferably  $1 \times 10^{-4}$  to  $1 \times 10^{-1}$  mol per mol of silver in the layer, and more preferably  $1 \times 10^{-3}$  to  $5 \times 10^{-2}$  mol per mol of silver in the layer.

The pKa of the compound of general formula (M) or (C) is determined by the following method. 0.5 milliliters (mL) of 1N sodium chloride aqueous solution is added to 100 mL of an aqueous solution containing tetrahydrofuran, in which 0.01 millimole of a coupler is dissolved, and water at 6:4 (wt. ratio). While the solution is stirred under atmosphere of nitrogen gas, titration is carried out using an aqueous 0.5N potassium hydroxide solution. In the titration curve plotted using the dropping amount of the aqueous potassium hydroxide solution on the horizontal axis, and pH value on the vertical axis, the pH at the inflection point is regarded as pKa. If there are a plurality of inflection points, i.e., the coupler has a dissociation site, in addition to the coupling-active position, an ultraviolet absorption spectrum is monitored simultaneously, and the variation of absorption of a coupler anion (dissociation form at the coupling-active position) in the vicinity of 260 to

350 nm is determined, thereby determining the inflection point.

The pKa of the compound of general formula (M) or (C) is preferably 6.0 to 8.4, and more preferably, 7.5 to 8.3.

The change of a film pAg ( $\Delta pAg_F$ ) caused by addition of the compound of general formula (M) or (C) is determined by the following method.

The change of a film pAg ( $\Delta pAg_F$ ) caused by addition of the compound of general formula (M) or (C) is determined by the difference in film pAg value from the case where the following evaluation photosensitive material (A) is prepared and no compound of formula (M) is added. The film pAg value is obtained by immersing the photosensitive material of a size of 8cm×12cm in 100 mL of the following buffer whose pH is adjusted to 10 for 5 minutes, and determining the pAg of the buffer using a silver electrode and comparison electrode (calomel electrode).

<Buffer Solution Preparation Method>

Boric acid	7.73 g
Potassium chloride	49.0 g
Potassium carbonate	17.3 g
1N potassium hydroxide aqueous solution	62.5 mL
Water to make	1,000 mL

The change of a film pAg caused by addition of the compound of general formula (M) or (C) is preferably 0

to 0.3, and more preferably, 0 to 0.25.

Evaluation Light-Sensitive Material (A)

(Support)

Cellulose triacetate

5 (Emulsion Layer)

Em-C in terms of silver 1.07 g/m<sup>2</sup>

Gelatin 2.33 g/m<sup>2</sup>

ExC-1 0.76 g/m<sup>2</sup>

ExC-4 0.42 g/m<sup>2</sup>

10 Tricresyl phosphate 0.62 g/m<sup>2</sup>

Compound of formula (M) or (C)  $3.9 \times 10^{-4}$  mol/m<sup>2</sup>

(Protective Layer)

Gelatin 2.00 g/m<sup>2</sup>

H-1 0.33 g/m<sup>2</sup>

15 B-2 (diameter of 1.7  $\mu$ m) 0.10 g/m<sup>2</sup>

B-2 (diameter of 1.7  $\mu$ m) 0.30 g/m<sup>2</sup>

B-3 0.10 g/m<sup>2</sup>

The characteristics of the emulsion Em-C and the structure of each compound used in the above evaluation photosensitive material (A) are shown in Example 1 described later.

20

The reactivity (CRV) of the compound of general formula (M) or (C) with an oxidized color developing agent is determined by the following method.

25

The evaluation photosensitive material (A) was exposed to white light, and was processed in the same manner as the processing method described in Example 1,

except that the process time of the color development step was changed to 1 minute and 15 seconds. The magenta density of the photosensitive material was determined and the cyan density was also determined.

5 The differences between the magenta density and cyan density of the photosensitive material and those of the photosensitive material containing no compound of ~~general~~ formulae (M) and (C) were determined.

10 With respect to the compound of formula (M), the difference in magenta density determined by the above method is regarded as CRV. With respect to the compound of formula (C), the difference in cyan density determined by the above method is regarded as CRV.

15 The CRV is preferably 0.01 to 0.10 in improving the speed/graininess, and more preferably, 0.01 to 0.05.

For the photosensitive material of the present invention, it is only required that at least one blue-sensitive, green-sensitive, and red-sensitive silver halide emulsion layer and nonsensitive layer be  
20 formed on a support. A typical example is a silver halide photosensitive material having, on its support, at least one blue-sensitive layer, at least one green-sensitive layer, at least one red-sensitive layer, each of which is constituted by a plurality of  
25 silver halide emulsion layers that are sensitive to essentially the same color but have different speeds, and at least one nonsensitive layer. This

light-sensitive layer includes a unit light-sensitive layer which is sensitive to one of blue light, green light and red light. In a multilayered silver halide color photosensitive material, these unit light-sensitive layers are generally arranged in the order of red-, green- and blue-sensitive layers from a support. However, according to the intended use, this arrangement order may be reversed, or light-sensitive layers sensitive to the same color can sandwich another light-sensitive layer sensitive to a different color. A nonsensitive layer may be formed between the silver halide light-sensitive layers and as the uppermost layer and the lowermost layer. These layers may contain, e.g., couplers to be described later, DIR compounds and color-mixing inhibitors. : As for a plurality of silver halide emulsion layers constituting respective unit light-sensitive layer, a two-layered structure of high- and low-speed emulsion layers can be preferably used in this order so as to the speed becomes lower toward the support as described in DE (German Patent) 1,121,470 or GB 923,045, the entire contents of which are incorporated herein by reference. Also, as described in JP-A's-57-112751, 62-200350, 62-206541 and 62-206543, the entire contents of which are incorporated herein by reference, layers may be arranged such that a low-speed emulsion layer is formed farther from a support and a high-speed layer is formed

closer to the support.

More specifically, layers can be arranged from the farthest side from a support in the order of low-speed blue-sensitive layer (BL)/high-speed blue-sensitive layer (BH)/high-speed green-sensitive layer (GH)/low-speed green-sensitive layer (GL)/high-speed red-sensitive layer (RH)/low-speed red-sensitive layer (RL), the order of BH/BL/GL/GH/RH/RL or the order of BH/BL/GH/GL/RL/RH.

Further, as described in JP-A-55-34932, the layers can be arranged from the farthest side from a support in the order of blue-sensitive layer/GH/RH/GL/RL. Also, as described in JP-A's-56-25738 and 62-63936, the entire contents of which are incorporated herein by reference, the layers can be arranged from the farthest side from a support, blue-sensitive layer/GL/RL/GH/RH.

As described in Jpn. Pat. Appln. KOKOKU Publication No. (hereinafter referred to as JP-B-) 55-34932, the entire contents of which are incorporated herein by reference, the layers may be arranged in the order of blue-sensitive layer/GH/RH/GL/RL from the farthest side from a support. Also, as described in JP-B-56-25738, the entire contents of which are incorporated herein by reference, the layers may be arranged in the order of blue-sensitive layer/GL/RL/GH/RH from the farthest side to the support.

As described in JP-B-49-15495, the entire contents



of which are incorporated herein by reference, three layers can be arranged such that a silver halide emulsion layer having the highest sensitivity is arranged as an upper layer, a silver halide emulsion layer having sensitivity lower than that of the upper layer is arranged as an interlayer, and a silver halide emulsion layer having sensitivity lower than that of the interlayer is arranged as a lower layer; i.e., three layers having different sensitivities can be arranged such that the sensitivity is sequentially decreased toward the support. Even when a layer structure is constituted by three layers having different sensitivities, these layers can be arranged in the order of medium-speed emulsion layer/high-speed emulsion layer/low-speed emulsion layer from the farthest side from a support in a layer sensitive to one color as described in JP-A-59-202464, the entire contents of which are incorporated herein by reference.

In addition, the order of high-speed emulsion layer/low-speed emulsion layer/medium-speed emulsion layer or low-speed emulsion layer/medium-speed emulsion layer/high-speed emulsion layer can be adopted.

Furthermore, the arrangement can be changed as described above even when four or more layers are formed.

The silver halide preferably used in the present invention is silver bromiodide, silver iodochloride,

or silver bromochloroiodide containing about 30 mol% or less of silver iodide. A particularly preferable silver halide is silver bromoiodide or silver bromochloroiodide containing about 2 to about 10 mol% of silver iodide.

Silver halide grains contained in the photographic emulsion can have regular crystals such as cubic, octahedral, or tetradecahedral crystals, ~~irregular~~ crystals such as spherical or tabular crystals, crystals having crystal defects such as twin planes, or composite shapes thereof.

The silver halide grain can be a fine grain having a grain size of about 0.2  $\mu\text{m}$  or less, or be a large grain having a projected area diameter of upto about 10  $\mu\text{m}$ , and an emulsion can be either a polydisperse or monodisperse emulsion.

A silver halide photographic emulsion which can be used in the present invention can be prepared by methods described in, e.g., "I. Emulsion preparation and types," Research Disclosure (RD) No. 17643 (December, 1978), pp. 22 and 23, "I. Emulsion preparation and types", and RD No. 18716 (November, 1979), page 648, and RD No. 307105 (November, 1989), pp. 863 to 865; P. Glafkides, "Chemie et Phisique Photographique", Paul Montel, 1967; G.F. Duffin, "Photographic Emulsion Chemistry", Focal Press, 1966; and V.L. Zelikman et al., "Making and Coating

Photographic Emulsion", Focal Press, 1964.

Monodisperse emulsions described in, e.g., U.S.P. Nos. 3,574,628 and 3,655,394, and GB1,413,748 are also preferable.

5           Tabular grains having an aspect ratio of 3 or more can also be used in the present invention. Tabular grains can be easily prepared by methods described in Gutoff, "Photographic Science and Engineering", Vol. 14, pp. 248 to 257 (1970); and U.S.P. Nos. 4,434,226,  
10           4,414,310, 4,433,048, and 4,439,520, and GB2,112,157.

          It has been found out that the compound of the present invention which improves the speed/graininess ratio exhibits the advantage in an especially great degree when the compound is used in the same layer of a  
15           photosensitive material as that containing tabular grains having an average aspect ratio of 8 or more. The average aspect ratio is preferably from 8 to 100, more preferably from 12 to 50.

          A crystal structure can be uniform, can have  
20           different halogen compositions in the interior and the surface layer thereof, or can be a layered structure. Alternatively, a silver halide having a different composition can be bonded by an epitaxial junction or a compound except for a silver halide such as silver  
25           rhodanide or lead oxide can be bonded. A mixture of grains having various types of crystal shapes can also be used.

The above emulsion preferably has a dislocation line. In particular, the tabular grains preferably have a dislocation line at a fringe portion. The dislocation line can be introduced by the following methods: a method of adding an aqueous solution containing an iodized alkali, etc., to form a silver-iodide-rich layer; a method of adding the AgI fine grains; and a method described in JP-A-323487.

The above emulsion can be any of a surface latent image type emulsion which mainly forms a latent image on the surface of a grain, an internal latent image type emulsion which forms a latent image in the interior of a grain, and another type of emulsion which has latent images on the surface and in the interior of a grain. However, the emulsion must be a negative type emulsion. The internal latent image type emulsion can be a core/shell internal latent image type emulsion described in JP-A-63-264740. A method of preparing this core/shell internal latent image type emulsion is described in JP-A-59-133542. Although the thickness of a shell of this emulsion depends on, e.g., development conditions, it is preferably 3 to 40 nm, and most preferably, 5 to 20 nm.

A silver halide emulsion is normally subjected to physical ripening, chemical ripening, and spectral sensitization steps before it is used. Additives for use in these steps are described in RD Nos. 17643,

18716, and 307105, and they are summarized in a table to be presented later.

In a photosensitive material of the present invention, it is possible to mix, in a single layer,  
5 two or more types of emulsions different in at least one of characteristics of a photosensitive silver halide emulsion, i.e., a grain size, grain size distribution, halogen composition, grain shape, and speed.

10 It is also possible to preferably use surface-fogged silver halide grains described in U.S.P. No. 4,082,553, internally fogged silver halide grains described in U.S.P. Nos. 4,626,498 and JP-A-59-214852, and colloidal silver, in sensitive silver halide  
15 emulsion layers and/or essentially non-sensitive hydrophilic colloid layers. The internally fogged or surface-fogged silver halide grain means a silver halide grain which can be developed uniformly (non-imagewise) regardless of whether the location is  
20 a non-exposed portion or an exposed portion of the photosensitive material. A method of preparing the internally fogged or surface-fogged silver halide grain is described in U.S.P. Nos. 4,626,498 and JP-A-59-214852. A silver halide which forms the core  
25 of an internally fogged core/shell type silver halide grain can have a different halogen composition. As the internally fogged or surface-fogged silver halide, any

of silver chloride, silver chlorobromide, silver bromoiodide, and silver bromochloroiodide can be used. The average grain size of these fogged silver halide grains is preferably 0.01 to 0.75  $\mu\text{m}$ , and most preferably, 0.05 to 0.6  $\mu\text{m}$ . The grain shape can be a regular grain shape. Although the emulsion can be a polydisperse emulsion, it is preferably a monodisperse emulsion (in which at least 95% in weight or number of grains of silver halide grains have grain sizes falling within the range of  $\pm 40\%$  of the average grain size).

In the present invention, it is preferable to use a nonsensitive fine grain silver halide. The nonsensitive fine grain silver halide preferably consists of silver halide grains which are not exposed during imagewise exposure for obtaining a dye image and are not essentially developed during development. These silver halide grains are preferably not fogged in advance. In the fine grain silver halide, the content of silver bromide is 0 to 100 mol%, and silver chloride and/or silver iodide can be added if necessary. The fine grain silver halide preferably contains 0.5 to 10 mol% of silver iodide. The average grain size (the average value of equivalent-circle diameters of projected areas) of the fine grain silver halide is preferably 0.01 to 0.5  $\mu\text{m}$ , and more preferably, 0.02 to 0.2  $\mu\text{m}$ .

The fine grain silver halide can be prepared

following the same procedures as for a common sensitive silver halide. The surface of each silver halide grain need not be optically sensitized nor spectrally sensitized. However, before the silver halide grains  
5 are added to a coating solution, it is preferable to add a well-known stabilizer such as a triazole-based compound, azaindene-based compound, benzothiazolium-  
-based compound, mercapto-based compound, or zinc  
compound. Colloidal silver can be added to this  
10 fine grain silver halide grain-containing layer.

The silver coating amount of a photosensitive material of the present invention is preferably  
8.0 g/m<sup>2</sup> or less.

Photographic additives usable in the present  
15 invention are also described in RD's, the entire contents of which are incorporated herein by reference, and the relevant portions are summarized in the following table.

20		Types of Additives	RD17643	RD18716	RD307105
	1.	Chemical sensitizers	page 23	page 648 right column	page 866
25	2.	Sensitivity increasing agents		page 648 right column	
30	3.	Spectral sensitizers, super sensitizers	pages 23 - 24	page 648, right column to page 649, right column	pages 866 -868
35	4.	Brighteners	page 24	page 647, right column	page 868

5	5.	Light absorbents, filter dyes, ultraviolet absorbents	pages 25 - 26	page 649, right column to page 650, left column	page 873
	6.	Binders	page 26	page 651, left column	pages 873 - 874
10	7.	Plasticizers, lubricants	page 27	page 650, right column	page 876
15	8.	Coating aids, surfactants	pages 26 - 27	page 650, right column	pages 875 - 876
	9.	Antistatic agents	page 27	page 650, right column	pages 876 - 877
20	10.	Matting agents			pages 878 - 879

Various dye forming couplers can be used in the photosensitive material of the present invention, and the following couplers are particularly preferable.

Yellow couplers: couplers represented by formulas (I) and (II) in EP 502,424A; couplers represented by formulas (1) and (2) in EP 513,496A (particularly Y-28 on page 18); a coupler represented by formula (I) in claim 1 of EP 568,037A; a coupler represented by general formula (I) in column 1, lines 45 to 55, in U.S.P. 5,066,576; a coupler represented by general formula (I) in paragraph 0008 of JP-A-4-274425; couplers described in claim 1 on page 40 in EP 498,381A1 (particularly D-35 on page 18); couplers represented by formula (Y) on page 4 in EP 447,969A1 (particularly Y-1 (page 17) and Y-54 (page 41)); and couplers represented by formulas (II) to (IV) in column 7, lines 36 to 58, in U.S.P. 4,476,219 (particularly



II-17, II-19 (column 17), and II-24 (column 19)), the entire contents of the above documents disclosing the yellow couplers are incorporated herein by reference.

5           Magenta couplers: JP-A-3-39737 (L-57 (page 11, lower right column), L-68 (page 12, lower right column), and L-77 (page 13, lower right column); [A-4]-63 (page 134), and [A-4]-73 and -75 (page 139) in EP No. 456,257; M-4 and -6 (page 26), and M-7 (page 27) in EP No. 486,965; M-45 (page 19) in EP No. 571,959A;  
10       (M-1) (page 6) in JP-A-5-204106; and M-22 in paragraph 0237 of JP-A-4-362631, the entire contents of the above documents disclosing the magenta couplers are incorporated herein by reference.

          Cyan couplers: CX-1, CX-3, CX-4, CX-5, CX-11,  
15       CX-12, CX-14, and CX-15 (pages 14 to 16) in JP-A-4-204843; C-7 and C-10 (page 35), C-34 and C-35 (page 37), and (I-1) and (I-17) (pages 42 and 43) in JP-A-4-43345; and couplers represented by general formulas (Ia) and (Ib) in claim 1 of JP-A-6-67385, the  
20       entire contents of the above documents disclosing the cyan couplers are incorporated herein by reference.

          Polymer couplers: P-1 and P-5 (page 11) in JP-A-2-44345, the entire contents of which are incorporated herein by reference.

25           Couplers for forming a colored dye with a proper diffusibility are preferably those described in U.S.P. No. 4,366,237, GB No. 2,125,570, EP No. 96,873B, and DE

No. 3,234,533, the entire contents of which are incorporated herein by reference.

As couplers for correcting the unnecessary absorption of a colored dye, preferred use is made of, besides the magenta colored yellow couplers of the present invention, yellow colored cyan couplers represented by formulas (CI), (CII), (CIII), and (CIV) described on page 5 in EP No. 456,257A1 (particularly YC-86 on page 84); yellow colored magenta couplers ExM-7 (page 202), Ex-1 (page 249), and EX-7 (page 251) described in EP No. 456,257A1; magenta colored cyan couplers CC-9 (column 8) and CC-13 (column 10) described in U.S.P. No. 4,833,069; (2) (column 8) in U.S.P. No. 4,837,136; and colorless masking couplers represented by formula (A) in claim 1 of WO No. 92/11575 (particularly compound examples on pages 36 to 45), the entire contents of all the documents disclosing the couplers for correcting the unnecessary absorption of a colored dye are incorporated herein by reference.

Examples of compounds (including couplers) that react with an oxidized color developing agent to release a photographically useful compound residue are as follows. Development inhibitor release compounds: compounds represented by formulas (I), (II), (III), and (IV) on page 11 of EP No. 378,236A1 (particularly T-101 (page 30), T-104 (page 31), T-113 (page 36), T-131

(page 45), T-144 (page 51), and T-158 (page 58)); a compound represented by formula (I) on page 7 of EP No. 436,938A2 (particularly D-49 (page 51)); a compound represented by formula (1) in EP No. 568,037A (particularly (23) (page 11)); and compounds represented by formulas (I), (II), and (III) on pages 5 and 6 of EP No. 440,195A2 (particularly I-(1) on page 29). Bleaching accelerator release compounds: compounds represented by formulas (I) and (I') on page 5 of EP No. 310,125A2 (particularly (60) and (61) on page 61); and compounds represented by formula (I) in claim 1 of JP-A-6-59411 (particularly (7) (page 7)). Ligand release compounds: compounds represented by LIG-X described in claim 1 of U.S.P. No. 4,555,478 (particularly compounds in column 12, lines 21 to 41). Leuco dye release compounds: compounds 1 to 6 in columns 3 to 8 of U.S.P. No. 4,749,641. Fluorescent dye release compounds: compounds represented by COUP-DYE in claim 1 of U.S.P. No. 4,774,181 (particularly compounds 1 to 11 in columns 7 to 10). Development accelerator or fogging agent release compounds: compounds represented by formulas (1), (2), and (3) in column 3 of U.S.P. No. 4,656,123 (particularly (I-22) in column 25); and ExZK-2 on page 75, lines 36 to 38, in EP No. 450,637A2. Compounds which release a group which does not function as a dye unless it splits off: compounds represented by

formula (I) in claim 1 of U.S.P. No. 4,857,447  
(particularly Y-1 to Y-19 in columns 25 to 36).

Preferable examples of additives other than  
couplers are as follows.

5           Dispersion mediums of an oil-soluble organic  
compound: P-3, P-5, P-16, P-19, P-25, P-30, P-42, P-49,  
P-54, P-55, P-66, P-81, P-85, P-86, and P-93 (pages 140  
to 144) in JP-A-62-215272. Impregnating latexes of  
an oil-soluble organic compound: latexes described  
10 in U.S.P. No. 4,199,363. Scavengers of an oxidized  
color developing agent: compounds represented  
by formula (I) in column 2, lines 54 to 62, in  
U.S.P. No. 4,978,606 (particularly I-(1), I-(2), I-(6),  
and I-(12) (columns 4 and 5)), and formulas in column 2,  
15 lines 5 to 10, in U.S.P. No. 4,923,787 (particularly  
compound 1 (column 3)). Stain inhibitors: formulas (I)  
to (III) on page 4, lines 30 to 33, particularly I-47,  
I-72, III-1, and III-27 (pages 24 to 48) in  
EP No. 298321A. Discoloration inhibitors: A-6, A-7,  
20 A-20, A-21, A-23, A-24, A-25, A-26, A-30, A-37, A-40,  
A-42, A-48, A-63, A-90, A-92, A-94, and A-164 (pages 69  
to 118) in EP No. 298,321A; II-1 to III-23,  
particularly III-10, in columns 25 to 38 of U.S.P.  
No. 5,122,444; I-1 to III-4, particularly II-2, on  
25 pages 8 to 12 in EP No. 471,347A; and A-1 to A-48,  
particularly A-39 and A-42, in columns 32 to 40 of  
U.S.P. No. 5,139,931. Materials which reduce the use

amount of a color enhancer or a color amalgamation inhibitor: I-1 to II-15, particularly I-46, on pages 5 to 24 in EP No. 411,324A. Formalin scavengers: SCV-1 to SCV-28, particularly SCV-8, on pages 24 to 29 in EP  
5 No. 477,932A. Film hardeners: H-1, H-4, H-6, H-8, and H-14 on page 17 in JP-A-1-214845; compounds (H-1 to H-54) represented by formulas (VII) to (XII) in columns  
~~13~~ 13 to 23 of U.S.P. No. 4,618,573; compounds (H-1 to H-76), particularly H-14, represented by formula (6) on  
10 page 8, lower right column, in JP-A-2-214852; and compounds described in claim 1 of U.S.P. No. 3,325,287. Development inhibitor precursors: P-24, P-37, and P-39  
(pages 6 and 7) in JP-A-62-168139; and compounds described in claim 1, particularly 28 and 29 in column  
15 7, of U.S.P. No. 5,019,492. Antiseptic agents and mildewproofing agents; I-1 to III-43, particularly II-1, II-9, II-10, II-18, and III-25, in columns 3 to 15 of U.S.P. No. 4,923,790. Stabilizers and antifoggants:  
I-1 to (14), particularly I-1, I-60, (2), and (13), in  
20 columns 6 to 16 of U.S.P. No. 4,923,793; and compounds 1 to 65, particularly compound 36, in columns 25 to 32 of U.S.P. No. 4,952,483. Chemical sensitizers:  
triphenylphosphine, selenide, and compound 50 in JP-A-5-40324. Dyes: a-1 to b-20, particularly a-1,  
25 a-12, a-18, a-27, a-35, a-36, and b-5, on pages 15 to 18 and V-1 to V-23, particularly V-1, on pages 27 to 29 in JP-A-3-156450; F-I-1 to F-II-43, particularly F-I-11

and F-II-8, on pages 33 to 55 in EP No. 445,627A; III-1 to III-36, particularly III-1 and III-3, on pages 17 to 28 in EP No. 457,153A; microcrystalline dispersions of Dye-1 to Dye-124 on pages 8 to 26 in WO No. 88/04794; compounds 1 to 22, particularly compound 1, on pages 6 to 11 in EP No. 319,999A; compounds D-1 to D-87 (pages 3 to 28) represented by formulas (1) to (3) in EP No. 519,306A; compounds 1 to 22 (columns 3 to 10) represented by formula (I) in U.S.P. No. 4,268,622; and compounds (1) to (31) (columns 2 to 9) represented by formula (I) in U.S.P. No. 4,923,788. UV absorbents: compounds (18b) to (18r) and 101 to 427 (pages 6 to 9) represented by formula (1) in JP-A-46-3335; compounds (3) to (66) (pages 10 to 44) represented by formula (I) and compounds HBT-1 to HBT-10 (page 14) represented by formula (III) in EP No. 520,938A; and compounds (1) to (31) (columns 2 to 9) represented by formula (1) in EP No. 521,823A.

The present invention can be applied to various color photosensitive materials such as color negative films for general purposes or cinemas, color reversal films for slides and TV, color paper, color positive films and color reversal paper. Moreover, the present invention is suitable to lens equipped film units described in JP-B-2-32615 and Jpn. Utility Model Appln. KOKOKU Publication No. 3-39784.

Supports which can be suitably used in the present

invention are described in, e.g., RD. No. 17643, page 28; RD. No. 18716, from the right column of page 647 to the left column of page 648; and RD. No. 307105, page 879.

5           The specific speed in the present invention is determined by the method described in JP-A-63-236035. This determination method is based on JIS K 7614-1981. This method is substantially the same as the JIS determination method except in the points that the  
10   development process is completed within 30 minutes to 6 hours after sensitometric exposure, and the development process is based on the Fuji color standard processing formula CN-16.

          In the photosensitive material of the present  
15   invention, the thicknesses from the light-sensitive silver halide layer, which is the closest to the support, to the surface of the photosensitive material is preferably 24  $\mu\text{m}$  or less, and more preferably 22  $\mu\text{m}$  or less. The film swelling speed  $T_{1/2}$  is preferably 30  
20   sec or less, and more preferably, 20 sec or less. The film swelling speed  $T_{1/2}$  is defined as the time that, when the saturation film thickness means 90% of the maximum swollen film thickness realized by the processing in a color developing solution at 30°C for  
25   3 min 15 sec, spent for the film thickness to reach 1/2 of the saturation film thickness. The film thickness means one measured under moisture conditioning at 25°C

and at a relative humidity of 55% (two days). The film swelling speed  $T_{1/2}$  can be measured by using a swellometer described in A. Green et al., Photogr. Sci. Eng., Vol. 19, No. 2, pp. 124 to 129. The film swelling speed  $T_{1/2}$  can be regulated by adding a film hardening agent to gelatin as a binder or by changing aging conditions after coating. The swelling ratio preferably ranges from 150 to 400%. The swelling ratio can be calculated from the maximum swollen film thickness measured under the above conditions in accordance with the formula:

[maximum swollen film thickness - film thickness] / film thickness.

In the photosensitive material of the present invention, hydrophilic colloid layers (called "back layers") having a total dried film thickness of 2 to 20  $\mu\text{m}$  are preferably formed on the side opposite to the side having emulsion layers. The back layers preferably contain the above light absorbent, filter dye, ultraviolet absorbent, antistatic agent, film hardener, binder, plasticizer, lubricant, coating aid and surfactant. The swelling ratio of the back layers is preferably 150% to 500%.

The photosensitive material of the present invention can be developed by conventional methods described in RD. No. 17643, pages 28 and 29; RD. No. 18716, page 651, left to right columns; and RD



No. 307105, pages 880 and 881.

The color negative film processing solution for use in the present invention will be described below.

The compounds listed in page 9, right upper column,  
5 line 1 to page 11, left lower column, line 4 of  
JP-A-4-121739 can be used in the color developing  
solution for use in the present invention.  
Preferred color developing agents for use in  
especially rapid processing are 2-methyl-4-[N-ethyl-N-  
10 (2-hydroxyethyl)amino]aniline,  
2-methyl-4-[N-ethyl-N-(3-hydroxypropyl)amino]aniline  
and 2-methyl-4-[N-ethyl-N-(4-hydroxybutyl)amino]aniline.

These color developing agents are preferably used  
in an amount of 0.01 to 0.08 mol, more preferably 0.015  
15 to 0.06 mol, and much more preferably 0.02 to 0.05 mol  
per liter (L) of the color developing solution.  
The replenisher of the color developing solution  
preferably contains the color developing agent in  
an amount corresponding to 1.1 to 3 times the above  
20 concentration, more preferably 1.3 to 2.5 times the  
above concentration.

Hydroxylamine can widely be used as preservatives  
of the color developing solution. When enhanced  
preserving properties are required, it is preferred to  
25 use hydroxylamine derivatives having substituents for  
example, alkyl, hydroxyalkyl, sulfoalkyl and  
carboxyalkyl groups, examples of which include

N,N-di(sulfoethyl)hydroxylamine,  
monomethylhydroxylamine, dimethylhydroxylamine,  
monoethylhydroxylamine, diethylhydroxylamine and  
N,N-di(carboxyethyl)hydroxylamine. Of these,  
5 N,N-di(sulfoethyl)hydroxylamine is most preferred.  
Although these may be used in combination with the  
hydroxylamine, it is preferred that one or at least two  
members thereof be used in place of the hydroxylamine.

These preservatives are preferably used in an  
10 amount of 0.02 to 0.2 mol, more preferably 0.03 to  
0.15 mol, and most preferably 0.04 to 0.1 mol per liter  
of the color developing solution. The replenisher of  
the color developing solution preferably contains the  
preservative in an amount corresponding to 1.1 to  
15 3 times the concentration of the mother liquor  
(processing tank solution) as in the color developing  
agent.

Sulfurous salts are used as tarring preventives  
for the oxidized color developing agent in the color  
20 developing solution. Each sulfurous salt is preferably  
used in the color developing solution in an amount of  
0.01 to 0.05 mol, more preferably 0.02 to 0.04 mol per  
liter, and is preferably used in the replenisher in an  
amount corresponding to 1.1 to 3 times the above  
25 concentration.

The pH value of the color developing solution  
preferably ranges from 9.8 to 11.0, more preferably

from 10.0 to 10.5. That of the replenisher is preferably set at 0.1 to 1.0 higher than the above value. Common buffers such as carbonate, phosphonate, sulfosalicylate and borate are used for stabilizing the  
5 above pH value.

Although the amount of the replenisher of the color developing solution preferably ranges from 80 to ~~1300~~ mL per m<sup>2</sup> of the photosensitive material, it is desired that the amount be smaller from the viewpoint  
10 of reducing environmental pollution load. Specifically, the amount of the replenisher more preferably ranges from 80 to 600 mL, most preferably from 80 to 400 mL.

Although the bromide ion concentration of the color developing solution generally ranges from 0.01 to  
15 0.06 mol per liter, it is preferred that the above concentration be set at 0.015 to 0.03 mol per liter for inhibiting fog while maintaining sensitivity to thereby improve discrimination and for bettering graininess. When the bromide ion concentration is set so as to fall  
20 within the above range, the replenisher preferably contains bromide ion in a concentration as calculated by the following formula. However, when C is negative, it is preferred that no bromide ion be contained in the replenisher.

25 
$$C = A - W/V$$

wherein

C: bromide ion concentration of the color developing

replenisher (mol/L),

A: target bromide ion concentration of the color  
developing solution (mol/L),

V: amount of color developing replenisher supplied per  
5 m<sup>2</sup> of the photosensitive material (L).

Development accelerators such as pyrazolidones  
represented by 1-phenyl-3-pyrazolidone and 1-phenyl-2-  
~~methoxy~~1-2-hydroxymethyl-3-pyrazolidone and thioether  
compounds represented by 3,6-dithia-1,8-octanediol are  
10 preferably used for means for enhancing sensitivity  
when the amount of the replenisher has been reduced or  
when a high bromide ion concentration has been set.

Compounds and processing conditions described on  
page 4, left lower column, line 16 to page 7, left  
15 lower column, line 6 of JP-A-4-125558 can be applied to  
the processing solution having bleaching capability for  
use in the present invention.

Bleaching agents having redox potentials of at  
least 150 mV are preferably used. Specifically,  
20 suitable examples thereof are those described in  
JP-A-5-72694 and JP-A-5-173312, and especially suitable  
examples thereof are 1,3-diaminopropanetetraacetic acid  
and ferric complex salts of Example 1 compounds listed  
on page 7 of JP-A-5-173312.

25 For improving the biodegradability of the  
bleaching agent, it is preferred that ferric complex  
salts of compounds listed in JP-A's-4-251845, and

4-268552, EP Nos. 588,289, and 591,934 and

JP-A-6-208213 be used as the bleaching agent.

The concentration of the above bleaching agent preferably ranges from 0.05 to 0.3 mol per liter of the

5 solution having bleaching capability, and it is especially preferred that a design be made at 0.1 to 0.15 mol per liter for reducing the discharge to the environment. When the solution having bleaching

capability is a bleaching solution, a bromide is preferably incorporated therein in an amount of 0.2 to 10 1 mol; more preferably 0.3 to 0.8 mol per liter.

Each component is incorporated in the replenisher of the solution having bleaching capability fundamentally in a concentration calculated by the following formula. This enables holding the 15 concentration of the mother liquor constant.

$$C_R = C_T \times (V_1 + V_2) / V_1 + C_P$$

$C_R$ : concentration of each component in the replenisher,

$C_T$ : concentration of the component in the mother liquor (processing tank solution), 20

$V_1$ : amount of replenisher having bleaching capability supplied per  $m^2$  of photosensitive material (mL), and

$V_2$ : amount carried from previous bath by 1  $m^2$  of photosensitive material (mL).

25 In addition, a pH buffer is preferably incorporated in the bleaching solution, and it is especially preferred to incorporate a dicarboxylic acid

of low order such as succinic acid, maleic acid, malonic acid, glutaric acid or adipic acid. It is also preferred to use common bleaching accelerators listed in JP-A-53-95630, RD No. 17129 and U.S.P. No. 3,893,858.

5           The bleaching solution is preferably replenished with 50 to 1000 mL, more preferably 80 to 500 mL, and much more preferably 100 to 300 mL, of a bleaching ~~replenisher~~ per m<sup>2</sup> of the photosensitive material. Further, the bleaching solution is preferably aerated.

10           Compounds and processing conditions described on page 7, left lower column, line 10 to page 8, right lower column, line 19 of JP-A-4-125558 can be applied to a processing solution having fixing capability.

15           For enhancing the fixing velocity and preservability, it is especially preferred to incorporate compounds represented by the general formulae (I) and (II) of JP-A-6-301169 either individually or in combination in the processing solution having fixing capability. Further, the use of  
20           p-toluenesulfinic salts and sulfinic acids listed in JP-A-1-224762 is preferred from the viewpoint of enhancing the preservability.

25           Although the incorporation of an ammonium as a cation in the solution having bleaching capability or solution having fixing capability is preferred from the viewpoint of enhancing the bleach ability, it is preferred that the amount of ammonium be reduced or

brought to nil from the viewpoint of minimizing environmental pollution.

Conducting jet agitation described in JP-A-1-309059 is especially preferred in the bleach,  
5 bleach-fix and fixation steps.

The amount of replenisher supplied in the bleach-fix or fixation step is in the range of 100 to 1000 mL, preferably 150 to 700 mL, and especially preferably 200 to 600 mL, per m<sup>2</sup> of the photosensitive material.

10 Silver is preferably recovered by installing any of various silver recovering devices in an in-line or off-line mode in the bleach-fix or fixation step. In-line installation enables processing with the silver concentration of the solution lowered, so that the  
15 amount of replenisher can be reduced. It is also suitable to conduct an off-line silver recovery and recycle residual solution for use as a replenisher.

The bleach-fix and fixation steps can each be constructed by a plurality of processing tanks.  
20 Preferably, the tanks are provided with cascade piping and a multistage counterflow system is adopted. A 2-tank cascade structure is generally effective from the viewpoint of a balance with the size of the developing machine. The ratio of processing time in  
25 the former-stage tank to that in the latter-stage tank is preferably in the range of 0.5:1 to 1:0.5, more preferably 0.8:1 to 1:0.8.

From the viewpoint of enhancing the preservability, it is preferred that a chelating agent which is free without forming any metal complex be present in the bleach-fix and fixing solutions. Biodegradable chelating agents described in connection with the bleaching solution are preferably used as such a chelating agent.

~~JP-A-4-125558~~ Descriptions made on page 12, right lower column, line 6 to page 13, right lower column, line 16 of JP-A-4-125558 mentioned above can preferably be applied to water washing and stabilization steps. In particular, with respect to stabilizing solutions, the use of azolylmethylamines described in EP Nos. 504,609 and 519,190 and N-methylolazoles described in JP-A-4-362943 in place of formaldehyde and the dimerization of magenta coupler into a surfactant solution not containing an image stabilizer such as formaldehyde are preferred from the viewpoint of protecting working environment.

Further, stabilizing solutions described in JP-A-6-289559 can preferably be used for reducing the adhesion of refuse to a magnetic recording layer applied to the photosensitive material.

The replenishing amount of water washing and stabilizing solutions is preferably in the range of 80 to 1000 mL, more preferably 100 to 500 mL, and much more preferably 150 to 300 mL, per m<sup>2</sup> of the



photosensitive material from the viewpoint that water washing and stabilizing functions are ensured and that the amount of waste solution is reduced to contribute to environment protection. In the processing with the  
5 above replenishing amount, any of known mildewproofing agents such as thiabenzazole, 1,2-benzisothiazolin-3-one and 5-chloro-2-methylisothiazolin-3-one and ~~antibiotics~~ antibiotics such as gentamicin is preferably added, or water deionized by the use of, for example, an ion  
10 exchange resin is preferably used, for preventing the breeding of bacteria and mildew. The use of deionized water in combination with a mildewproofing agent and an antibiotic is more effective than individual uses.

With respect to the solution placed in the water  
15 washing or stabilizing solution tank, it is also preferred that the replenishing amount be reduced by conducting a reverse osmosis membrane treatment as described in JP-A's-3-46652, 3-53246, 3-55542, 3-121448 and 3-126030. A low-pressure reverse osmosis membrane  
20 is preferably used in the above treatment.

In the processing of the present invention, it is especially preferred that an evaporation correction of processing solution be carried out as disclosed in JIII  
(Japan Institute of Invention and Innovation) Journal  
25 of Technical Disclosure No. 94-4992. In particular, the method in which a correction is effected with the use of information on the temperature and humidity of

developing machine installation environment in accordance with Formula 1 on page 2 thereof is preferred. Water for use in the evaporation correction is preferably harvested from the washing replenishing tank. In that instance, deionized water is preferably used as the washing replenishing water.

Processing agents set forth on page 3, right column, line 15 to page 4, left column, line 32 of the above journal of technical disclosure are preferably used in the present invention. Film processor described on page 3, right column, lines 22 to 28 thereof is preferably used as the developing machine in the processing of the present invention.

Specific examples of processing agents, automatic developing machines and evaporation correction schemes preferably employed in carrying out the present invention are described on page 5, right column, line 11 to page 7, right column, last line of the above journal of technical disclosure.

The processing agent for use in the present invention may be supplied in any form, for example, a liquid agent with the same concentration as in use or concentrated one, granules, powder, tablets, a paste or an emulsion. For example, a liquid agent stored in a container of low oxygen permeability is disclosed in JP-A-63-17453, vacuum packed powder or granules in JP-A's-4-19655 and 4-230748, granules containing a

water soluble polymer in JP-A-4-221951, tablets in JP-A-51-61837 and JP-A-6-102628 and a paste processing agent in PCT National Publication 57-500485. Although any of these can be suitably used, from the viewpoint of easiness in use, it is preferred to employ a liquid prepared in the same concentration as in use in advance.

The container for storing the above processing agent is composed of, for example, any one or a mixture of polyethylene, polypropylene, polyvinyl chloride, polyethylene terephthalate and nylon. A selection is made in accordance with the required level of oxygen permeability. A material of low oxygen permeability is preferably used for storing an easily oxidized liquid such as a color developing solution, which is, for example, polyethylene terephthalate or a composite material of polyethylene and nylon. It is preferred that each of these materials be used in the container at a thickness of 500 to 1500  $\mu\text{m}$  so that the oxygen permeability therethrough is 20 mL/m<sup>2</sup> 24hrs atm or less.

The processing solution for color reversal film to be employed in the present invention will be described below.

With respect to the processing for color reversal film, detailed descriptions are made in Public Technology No. 6 (April 1, 1991) issued by Aztek, page 1, line 5 to page 10, line 5 and page 15, line 8 to page 24, line 2, any of which can be preferably

applied thereto.

In the color reversal film processing, an image stabilizer is added to a conditioning bath or a final bath. Examples of suitable image stabilizers include formalin, formaldehyde sodium bisulfite and N-methylolazoles. Formaldehyde sodium bisulfite and N-methylolazoles are preferred from the viewpoint of working environment, Among the N-methylolazoles, N-methyloltriazole is especially preferred. The contents of descriptions on color developing solution, bleaching solution, fixing solution and washing water made in connection with the processing of color negative films are also preferably applicable to the processing of color reversal films.

Processing agent E-6 available from Eastman Kodak and processing agent CR-56 available from Fuji Photo Film Co., Ltd. can be mentioned as preferred color reversal film processing agents including the above feature.

The magnetic recording layer for use in the present invention will be described below.

The magnetic recording layer is obtained by coating on a support with a water-base or organic solvent coating liquid having magnetic material grains dispersed in a binder.

Suitable magnetic material grains can be composed of any of ferromagnetic iron oxides such as  $\gamma$   $\text{Fe}_2\text{O}_3$ , Co coated  $\gamma$   $\text{Fe}_2\text{O}_3$ , Co coated magnetite, Co

containing magnetite, ferromagnetic chromium dioxide, ferromagnetic metals, ferromagnetic alloys, Ba ferrite of hexagonal system, Sr ferrite, Pb ferrite and Ca ferrite. Of these, Co coated ferromagnetic iron oxides such as Co coated  $\gamma$   $\text{Fe}_2\text{O}_3$  are preferred. The configuration thereof may be any of acicular, rice grain, spherical, cubic and plate shapes. ~~The~~ specific surface area is preferably at least  $20 \text{ m}^2/\text{g}$ , more preferably at least  $30 \text{ m}^2/\text{g}$  in terms of SBET.

The saturation magnetization ( $\sigma_s$ ) of the ferromagnetic material preferably ranges from  $3.0 \times 10^4$  to  $3.0 \times 10^5 \text{ A/m}$ , more preferably from  $4.0 \times 10^4$  to  $2.5 \times 10^5 \text{ A/m}$ . The ferromagnetic material grains may have their surface treated with silica and/or alumina or an organic material. Further, the magnetic material grains may have their surface treated with a silane coupling agent or a titanium coupling agent as described in JP-A-6-161032. Still further, use can be made of magnetic material grains having their surface coated with an organic or inorganic material as described in JP-A's-4-259911 and 5-81652.

The binder for use in the magnetic material grains can be composed of any of natural polymers (e.g., cellulose derivatives and sugar derivatives), acid-, alkali- or bio-degradable polymers, reactive resins, radiation curable resins, thermosetting resins

and thermoplastic resins listed in JP-A-4-219569 and mixtures thereof. The Tg of each of the above resins ranges from -40 to 300°C and the weight average molecular weight thereof ranges from 2 thousand to 1 million. For example, vinyl copolymers, cellulose derivatives such as cellulose diacetate, cellulose triacetate, cellulose acetate propionate, cellulose acetate butyrate and cellulose tripropionate, acrylic resins and polyvinylacetal resins can be mentioned as suitable binder resins. Gelatin is also a suitable binder resin. Of these, cellulose di(tri)acetate is especially preferred. The binder can be cured by adding an epoxy, aziridine or isocyanate crosslinking agent. Suitable isocyanate crosslinking agents include, for example, isocyanates such as tolylene diisocyanate, 4,4'-diphenylmethane diisocyanate, hexamethylene diisocyanate and xylylene diisocyanate, reaction products of these isocyanates and polyalcohols (e.g., reaction product of 3 mol of tolylene diisocyanate and 1 mol of trimethylolpropane), and polyisocyanates produced by condensation of these isocyanates, as described in, for example, JP-A-6-59357.

The method of dispersing the magnetic material in the above binder preferably comprises using a kneader, a pin type mill and an annular type mill either individually or in combination as described in

JP-A-6-35092. Dispersants listed in JP-A-5-088283 and other common dispersants can be used. The thickness of the magnetic recording layer ranges from 0.1 to 10  $\mu\text{m}$ , preferably 0.2 to 5  $\mu\text{m}$ , and more preferably from 0.3 to 3  $\mu\text{m}$ . The weight ratio of magnetic material grains to binder is preferably in the range of 0.5:100 to 60:100, more preferably 1:100 to 30:100. The coating amount of magnetic material grains ranges from 0.005 to 3  $\text{g}/\text{m}^2$ , preferably from 0.01 to 2  $\text{g}/\text{m}^2$ , and more preferably from 0.02 to 0.5  $\text{g}/\text{m}^2$ . The transmission yellow density of the magnetic recording layer is preferably in the range of 0.01 to 0.50, more preferably 0.03 to 0.20, and most preferably 0.04 to 0.15. The magnetic recording layer can be applied to the back of a photographic support in its entirety or in striped pattern by coating or printing. The magnetic recording layer can be applied by the use of, for example, an air doctor, a blade, an air knife, a squeeze, an immersion, reverse rolls, transfer rolls, a gravure, a kiss, a cast, a spray, a dip, a bar or an extrusion. Coating liquids set forth in JP-A-5-341436 are preferably used.

The magnetic recording layer may also be provided with, for example, lubricity enhancing, curl regulating, antistatic, sticking preventive and head polishing functions, or other functional layers may be disposed to impart these functions. An abrasive of grains whose at least one member is nonspherical

inorganic grains having a Mohs hardness of at least 5 is preferred. The nonspherical inorganic grains are preferably composed of fine grains of any of oxides such as aluminum oxide, chromium oxide, silicon dioxide and titanium dioxide; carbides such as silicon carbide and titanium carbide; and diamond. These abrasives may have their surface treated with a silane coupling agent or a titanium coupling agent. The above grains may be added to the magnetic recording layer, or the magnetic recording layer may be overcoated with the grains (e.g., as a protective layer or a lubricant layer). The binder which is used in this instance can be the same as mentioned above and, preferably, the same as the that of the magnetic recording layer. The lightsensitive material having the magnetic recording layer is described in U.S.P.'s 5,336,589, 5,250,404, 5,229,259, and 5,215,874 and EP No. 466,130.

The polyester support for use in the present invention will be described below. Particulars thereof together with the below mentioned lightsensitive material, processing, cartridge and working examples are specified in Journal of Technical Disclosure No. 94-6023 (issued by Japan Institute of Invention and Innovation on March 15, 1994). The polyester for use in the present invention is prepared from a diol and an aromatic dicarboxylic acid as essential components. Examples of suitable aromatic



dicarboxylic acids include 2,6-, 1,5-, 1,4- and  
2,7-naphthalenedicarboxylic acids, terephthalic  
acid, isophthalic acid and phthalic acid, and  
examples of suitable diols include diethylene glycol,  
5 triethylene glycol, cyclohexanedimethanol, bisphenol A  
and other bisphenols. The resultant polymers include  
homopolymers such as polyethylene terephthalate,  
~~poly~~ethylene naphthalate and polycyclohexanedimethanol  
terephthalate. Polyesters containing  
10 2,6-naphthalenedicarboxylic acid in an amount of 50 to  
100 mol% are especially preferred. Polyethylene  
2,6-naphthalate is most preferred. The average  
molecular weight thereof ranges from approximately  
5,000 to 200,000. The T<sub>g</sub> of the polyester of the  
15 present invention is at least 50°C, preferably at  
least 90°C.

The polyester support is subjected to heat  
treatment at a temperature of from 40°C to less than T<sub>g</sub>,  
preferably from T<sub>g</sub> minus 20°C to less than T<sub>g</sub>, in order  
20 to suppress curling. This heat treatment may be  
conducted at a temperature held constant within the  
above temperature range or may be conducted while  
cooling. The period of heat treatment ranges from 0.1  
to 1500 hr, preferably 0.5 to 200 hr. The support may  
25 be heat treated either in the form of a roll or while  
being carried in the form of a web. The surface form  
of the support may be improved by rendering the surface

irregular (e.g., coating with conductive inorganic fine grains of  $\text{SnO}_2$ ,  $\text{Sb}_2\text{O}_5$ , etc.). Moreover, a scheme is desired such that edges of the support are knurled so as to render only the edges slightly high, thereby preventing photographing of core sections. The above heat treatment may be carried out in any of stages after support film formation, after surface treatment, after back layer application (e.g., application of an antistatic agent or a lubricant) and after undercoating application. The heat treatment is preferably performed after antistatic agent application.

An ultraviolet absorber may be milled into the polyester. Light piping can be prevented by milling, into the polyester, dyes and pigments commercially available as polyester additives, such as Diaresin produced by Mitsubishi Chemical Industries, Ltd. and Kayaset produced by NIPPON KAYAKU CO., LTD.

In the present invention, a surface treatment is preferably conducted for bonding a support and a lightsensitive material constituting layer to each other. The surface treatment is, for example, a surface activating treatment such as chemical treatment, mechanical treatment, corona discharge treatment, flame treatment, ultraviolet treatment, high frequency treatment, glow discharge treatment, active plasma treatment, laser treatment, mixed acid treatment or ozone oxidation treatment. Of these surface

treatments, ultraviolet irradiation treatment, flame treatment, corona treatment and glow treatment are preferred.

Next, a subbing layer will be described. The subbing layer may be composed of a single layer or two or more layers. As the binder for the substratum, there can be mentioned not only copolymers prepared from monomers, as starting materials, selected from among vinyl chloride, vinylidene chloride, butadiene, methacrylic acid, acrylic acid, itaconic acid and maleic anhydride but also polyethyleneimine, an epoxy resin, a grafted gelatin, nitrocellulose and gelatin. Resorcin or p-chlorophenol is used as a support swelling compound. A gelatin hardener such as a chromium salt (e.g., chrome alum), an aldehyde (e.g., formaldehyde or glutaraldehyde), an isocyanate, an active halogen compound (e.g., 2,4-dichloro-6-hydroxy-S-triazine), an epichlorohydrin resin or an active vinyl sulfone compound can be used in the subbing layer. Also,  $\text{SiO}_2$ ,  $\text{TiO}_2$ , inorganic fine grains or polymethyl methacrylate copolymer fine grains (0.01 to 10  $\mu\text{m}$ ) may be incorporated therein as a matting agent.

Further, an antistatic agent is preferably used in the present invention. Examples of suitable antistatic agents include carboxylic acids and carboxylic salts, sulfonic acid salt containing polymers, cationic polymers and ionic surfactant compounds.

Most preferred as the antistatic agent are fine grains of at least one crystalline metal oxide selected from among ZnO, TiO<sub>2</sub>, SnO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, In<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, MgO, BaO, MoO<sub>3</sub> and V<sub>2</sub>O<sub>5</sub> having a volume resistivity of 5 10<sup>7</sup> Ω·cm or less, preferably 10<sup>5</sup> Ω·cm or less, and having a grain size of 0.001 to 1.0 μm or a composite oxide thereof (Sb, P, B, In, S, Si, C, etc.) and fine grains of sol form metal oxides or composite oxides thereof. The content thereof in the lightsensitive 10 material is preferably in the range of 5 to 500 mg/m<sup>2</sup>, more preferably 10 to 350 mg/m<sup>2</sup>. The ratio of amount of conductive crystalline oxide or composite oxide thereof to binder is preferably in the range of 1/300 to 100/1, more preferably 1/100 to 100/5.

15 It is preferred that the lightsensitive material of the present invention have lubricity. The lubricant containing layer is preferably provided on both the lightsensitive layer side and the back side. Preferred lubricity ranges from 0.25 to 0.01 in terms of dynamic 20 friction coefficient. The measured lubricity is a value obtained by conducting a carriage on a stainless steel ball of 5 mm in diameter at 60 cm/min (25°C, 60% RH). In this evaluation, value of approximately the same level is obtained even when the opposite 25 material is replaced by the lightsensitive layer side.

The lubricant which can be used in the present invention is, for example, a polyorganosiloxane,

a higher fatty acid amide, a higher fatty acid metal salt or an ester of higher fatty acid and higher alcohol. Examples of suitable polyorganosiloxanes include polydimethylsiloxane, polydiethylsiloxane, 5 polystyrylmethylsiloxane and polymethylphenylsiloxane. The lubricant is preferably added to the back layer or the outermost layer of the emulsion layer. Especially, ~~polydimethylsiloxane~~ and an ester having a long chain alkyl group are preferred.

10 A matting agent is preferably used in the light-sensitive material of the present invention. Although the matting agent may be used on the emulsion side or the back side indiscriminately, it is especially preferred that the matting agent be added to the 15 outermost layer of the emulsion side. The matting agent may be soluble in the processing solution or insoluble in the processing solution, and it is preferred to use the soluble and insoluble matting agents in combination. For example, polymethyl 20 methacrylate, poly(methyl methacrylate/methacrylic acid) (9/1 or 5/5 in molar ratio) and polystyrene grains are preferred. The grain size thereof preferably ranges from 0.8 to 10  $\mu\text{m}$ . Narrow grain size distribution thereof is preferred, and it is desired 25 that at least 90% of the whole number of grains be included in the range of 0.9 to 1.1 times the average grain size. Moreover, for enhancing the mat

properties, it is preferred that fine grains of  $0.8 \mu\text{m}$  or less be simultaneously added, which include, for example, fine grains of polymethyl methacrylate ( $0.2 \mu\text{m}$ ), poly(methyl methacrylate/methacrylic acid) (9/1 in molar ratio,  $0.3 \mu\text{m}$ ), polystyrene ( $0.25 \mu\text{m}$ ) and colloidal silica ( $0.03 \mu\text{m}$ ).

The film patrone employed in the present invention ~~will be~~ described below. The main material composing the patrone for use in the present invention may be a metal or a synthetic plastic.

Examples of preferable plastic materials include polystyrene, polyethylene, polypropylene and polyphenyl ether. The patrone for use in the present invention may contain various types of antistatic agents and can preferably contain, for example, carbon black, metal oxide grains, nonionic, anionic, cationic or betaine type surfactants and polymers. Such an antistatic patrone is described in JP-A's-1-312537 and 1-312538. The resistance thereof at  $25^{\circ}\text{C}$  in 25% RH is preferably  $10^{12} \Omega$  or less. The plastic patrone is generally molded from a plastic having carbon black or a pigment milled thereinto for imparting light shielding properties. The patrone size may be the same as the current size 135, or for miniaturization of cameras, it is advantageous to decrease the diameter of the 25 mm cartridge of the current size 135 to 22 mm or less. The volume of the case of the patrone is preferably

30 cm<sup>3</sup> or less, more preferably 25 cm<sup>3</sup> or less. The weight of the plastic used in each patrone or patrone case preferably ranges from 5 to 15g.

5 The patrone for use in the present invention may be one capable of feeding a film out by rotating a spool. Further, the patrone may be so structured that a film front edge is accommodated in the main ~~frame~~ of the patrone and that the film front edge is fed from a port part of the patrone to the outside by  
10 rotating a spool shaft in a film feeding out direction. These are disclosed in U.S.P.'s 4,834,306 and 5,226,613. The photographic film for use in the present invention may be a generally so termed raw stock having not yet been developed or a developed  
15 photographic film. The raw stock and the developed photographic film may be accommodated in the same new patrone or in different patrones.

A color photosensitive material of the present invention is also suitably used as a negative film for  
20 an advanced photo system (to be referred to as an APS hereinafter). Examples are NEXIA A, NEXIA F, and NEXIA H (ISO 200, 100, and 400, respectively) manufactured by Fuji Photo Film Co., Ltd. (to be referred to as Fuji Film hereinafter). These films are so processed as to  
25 have an APS format and set in an exclusive cartridge. These APS cartridge films are loaded into APS cameras such as the Fuji Film EPION Series represented by the

EPION 300Z. A color photosensitive film of the present invention is also suited as a film with lens such as Fuji Film FUJICOLOR UTSURUNDESU SUPER SLIM.

5 A photographed film is printed through the following steps in a miniature laboratory system.

- (1) Reception (an exposed cartridge film is received from a customer)
- (2) Detaching step (the film is transferred from the cartridge to an intermediate cartridge for development)
- 10 (3) Film development
- (4) Reattaching step (the developed negative film is returned to the original cartridge)
- (5) Printing (prints of three types C, H, and P and an index print are continuously automatically printed
- 15 on color paper [preferably Fuji Film SUPER FA8])
- (6) Collation and shipment (the cartridge and the index print are collated by an ID number and shipped together with the prints)

As these systems, the Fuji Film MINILABO CHAMPION  
20 SUPER FA-298, FA-278, FA-258, FA-238 are preferable. Examples of a film processor are the FP922AL, FP562B, FP562BL, FP362B, and FP3622BL, and a recommended processing chemical is the FUJICOLOR JUST-IT CN-16L. Examples of a printer processor are the PP3008AR,  
25 PP3008A, PP1828AR, PP1828A, PP1258AR, PP1258A, PP728AR, and PP728A, and a recommended processing chemical is the FUJICOLOR JUST-IT CP-47L. A detacher used in the



detaching step and a reattacher used in the reattaching step are preferably the Fuji Film DT200 or DT100 and AT200 or AT100, respectively.

5       The APS can also be enjoyed by PHOTO JOY SYSTEM  
whose main component is the Fuji Film Aladdin 1000  
digital image scanner. For example, a developed APS  
cartridge film is directly loaded into the Aladdin  
1000, or image information of a negative film, positive  
film, or print is input to the Aladdin 1000 by using  
10   the FE-550 35-mm film scanner or the PE-550 flat head  
scanner. Obtained digital image data can be easily  
processed and edited. This data can be printed out by  
the NC-550AL digital color printer using a photo-fixing  
heat-sensitive color printing system or the  
15   PICTOROGRAPHY 3000 using a laser exposure thermal  
development transfer system, or by existing laboratory  
equipment through a film recorder. The Aladdin 1000  
can also output digital information directly to a  
floppy disk or Zip disk or to an CD-R via a CD writer.

20       In a home, a user can enjoy photographs on a TV  
set simply by loading a developed APS cartridge film  
into the Fuji Film Photo Player AP-1. Image informa-  
tion can also be continuously input to a personal  
computer by loading a developed APS cartridge film into  
25   the Fuji Film Photo Scanner AS-1. The Fuji Film Photo  
Vision FV-10 or FV-5 can be used to input a film,  
print, or three-dimensional object. Furthermore, image

information recorded in a floppy disk, Zip disk, CD-R,  
or hard disk can be variously processed on a computer  
by using the Fuji Film Photo Factory application  
software. The Fuji Film NC-2 or NC-2D digital color  
5 printer using a photo-fixing heat-sensitive color  
printing system is suited to outputting high-quality  
prints from a personal computer.

~~very~~ To keep developed APS cartridge films, the  
FUJICOLOR POCKET ALBUM AP-5 POP L, AP-1 POP L, or AP-1  
10 POP KG, or the CARTRIDGE FILE 16 is preferable.

#### Example

Examples of the present invention will be  
described below, which, however, in no way limit the  
scope of the present invention.

#### 15 Example 1

The support used in this example was prepared by  
the following method.

##### 1) First layer and substratum:

Both surfaces of a 90  $\mu\text{m}$  thick polyethylene  
20 naphthalate support were treated with glow discharge  
under such conditions that the treating ambient  
pressure was  $2.66 \times 10$  Pa, the  $\text{H}_2\text{O}$  partial pressure  
of ambient gas 75%, the discharge frequency 30 kHz,  
the output 2500 W, and the treating strength  
25  $0.5 \text{ kV} \cdot \text{A} \cdot \text{min}/\text{m}^2$ . This support was coated, in a coating  
amount of  $5 \text{ mL}/\text{m}^2$ , with a coating liquid of the  
following composition to provide the 1st layer in

accordance with the bar coating method described in JP-B-58-4589.

	Conductive fine grain dispersion	
	( $\text{SnO}_2/\text{Sb}_2\text{O}_5$ grain conc. 10% water	
5	dispersion, secondary agglomerate of	
	0.005 $\mu\text{m}$ grain size primary grains which	
	has an av. grain size of 0.05 $\mu\text{m}$ )	50 pts.wt.
	<del>WPC</del> Gelatin	0.5 pt.wt.
	Water	49 pts.wt.
10	Polyglycerol polyglycidyl ether	0.16 pt.wt.
	Polyoxyethylene sorbitan monolaurate	
	(polymn. degree 20)	0.1 pt.wt.

The support furnished with the first coating layer was wound round a stainless steel core of 20 cm diameter and heated at 110°C (T<sub>g</sub> of PEN support: 119°C) for 48 hr to thereby effect heat history annealing. The other side of the support opposite to the first layer was coated, in a coating amount of 10 mL/m<sup>2</sup>, with a coating liquid of the following composition to provide a substratum for emulsion in accordance with the bar coating method.

	Gelatin	1.01 pts.wt.
	Salicylic acid	0.30 pt.wt.
	Resorcin	0.40 pt.wt.
25	Polyoxyethylene nonylphenyl ether	
	(polymn. degree 10)	0.11 pt.wt.
	Water	3.53 pt.wt.

Methanol	84.57 pts.wt.
n-Propanol	10.08 pts.wt.

Furthermore, the following second layer and third layer were superimposed in this sequence on the first layer by coating. Finally, multilayer coating of a color negative photosensitive material of the composition indicated below was performed on the opposite side. Thus, a transparent magnetic recording medium with silver halide emulsion layers was obtained.

2) Second layer (transparent magnetic recording layer):

(1) Dispersion of magnetic substance:

1100 parts by weight of Co-coated  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> magnetic substance (average major axis length: 0.25  $\mu$ m, S<sub>BET</sub>: 39 m<sup>2</sup>/g, H<sub>c</sub>: 6.56×10<sup>4</sup> A/m,  $\sigma_s$ : 77.1 Am<sup>2</sup>/kg, and  $\sigma_r$ : 37.4 Am<sup>2</sup>/kg), 220 parts by weight of water and 165 parts by weight of silane coupling agent

(3-(poly(polymerization degree: 10)oxyethynyl)oxypropyltrimethoxysilane) were fed into an open kneader, and blended well for 3 hr. The resultant coarsely dispersed viscous liquid was dried at 70°C round the clock to thereby remove water, and heated at 110°C for 1 hr. Thus, surface treated magnetic grains were obtained.

Further, in accordance with the following recipe, a composition was prepared by blending by means of the open kneader once more for 4 hr:

Thus obtained surface treated

	magnetic grains	855g
	Diacetylcellulose	25.3g
	Methyl ethyl ketone	136.3g
5	Cyclohexanone	136.3g

Still further, in accordance with the following recipe, a composition was prepared by carrying out fine dispersion by means of a sand mill (1/4G sand mill) at 2000 rpm for 4 hr. Glass beads of 1 mm $\phi$  diameter were used as medium.

	Thus obtained blend liquid	45g
	Diacetylcellulose	23.7g
	Methyl ethyl ketone	127.7g
	Cyclohexanone	127.7g

Moreover, in accordance with the following recipe, a magnetic substance-containing intermediate liquid was prepared.

(2) Preparation of magnetic substance-containing intermediate liquid:

20	Thus obtained fine dispersion of magnetic substance	674g
	Diacetylcellulose soln. (solid content 4.34%, solvent: methyl ethyl ketone/cyclohexanone = 1/1)	24,280g
25	Cyclohexanone	46g

These were mixed together and agitated by means of a disperser to thereby obtain a "magnetic substance-

containing intermediate liquid".

An  $\alpha$ -alumina abrasive dispersion of the present invention was produced in accordance with the following recipe.

- 5           (a) Preparation of Sumicorundum AA-1.5 (average primary grain diameter: 1.5  $\mu\text{m}$ , specific surface area: 1.3  $\text{m}^2/\text{g}$ ) grain dispersion

	Sumicorundum AA-1.5	152g
	Silane coupling agent KBM903	
10	(produced by Shin- Etsu Silicone)	0.48g
	Diacetylcellulose soln. (solid content 4.5%, solvent: methyl ethyl ketone/cyclohexanone = 1/1)	
		227.52g

15           In accordance with the above recipe, fine dispersion was carried out by means of a ceramic-coated sand mill (1/4G sand mill) at 800 rpm for 4 hr. Zirconia beads of 1 mm $\phi$  diameter were used as medium.

(b) Colloidal silica grain dispersion (fine grains)

20           Use was made of "MEK-ST" produced by Nissan Chemical Industries, Ltd.

            This is a dispersion of colloidal silica of 0.015  $\mu\text{m}$  average primary grain diameter in methyl ethyl ketone as a dispersion medium, wherein the solid  
25           content is 30%.

(3) Preparation of a coating liquid for second layer:

Thus obtained magnetic substance  
containing intermediate liquid 19,053g  
Diacetylcellulose soln. 264g  
(solid content 4.5%, solvent: methyl ethyl  
5 ketone/cyclohexanone = 1/1)  
Colloidal silica dispersion "MEK-ST"  
(dispersion b, solid content: 30%) 128g  
AA-1.5 dispersion (dispersion a) 12g  
Millionate MR-400 (produced by Nippon  
10 Polyurethane) diluent 203g  
(solid content 20%, dilution solvent:  
methyl ethyl ketone/cyclohexanone = 1/1)  
Methyl ethyl ketone 170g  
Cyclohexanone 170g  
15 A coating liquid obtained by mixing and agitating  
these was applied in a coating amount of 29.3 mL/m<sup>2</sup>  
with the use of a wire bar. Drying was performed  
at 110°C. The thickness of magnetic layer after drying  
was 1.0 μm.  
20 3) Third layer (higher fatty acid ester sliding  
agent containing layer)  
(1) Preparation of raw dispersion of sliding agent  
The following liquid A was heated at 100°C to  
thereby effect dissolution, added to liquid B and  
25 dispersed by means of a high-pressure homogenizer,  
thereby obtaining a raw dispersion of sliding agent.

Liquid A:

Compd. of the formula:

$C_6H_{13}CH(OH)(CH_2)_{10}COOC_{50}H_{101}$  399 pts.wt.

Compd. of the formula:

$n-C_{50}H_{101}O(CH_2CH_2O)_{16}H$  171 pts.wt.

5 Cyclohexanone 830 pts.wt.

Liquid B:

Cyclohexanone 8600 pts.wt.

(2) Preparation of spherical inorganic grain dispersion

10 Spherical inorganic grain dispersion (c1) was prepared in accordance with the following recipe.

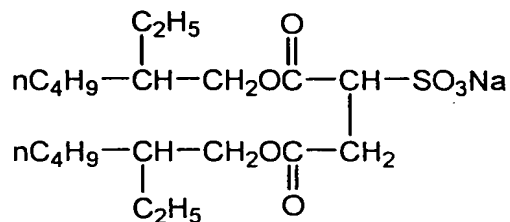
Isopropyl alcohol 93.54 pts.wt.

Silane coupling agent KBM903 (produced by Shin-Etsu Silicone) Compd. 1-1:

15  $(CH_3O)_3Si-(CH_2)_3-NH_2$  5.53 pts.wt.

Compound 1 2.93 pts.wt.

Compound 1



20 Seahostar KEP50 (amorphous spherical silica, av. grain size 0.5  $\mu m$ , produced by Nippon Shokubai Ltd. 88.00 pts.wt.

This composition was agitated for 10 min, and further the following was added.

Diacetone alcohol 252.93 pts.wt.

25 The resultant liquid was dispersed by means of



ultrasonic homogenizer "Sonifier 450 (manufactured by Branson)" for 3 hr while cooling with ice and stirring, thereby finishing spherical inorganic grain dispersion c1.

5 (3) Preparation of spherical organic polymer grain dispersion

Spherical organic polymer grain dispersion (c2) was prepared in accordance with the following recipe.

XC99-A8808 (produced by Toshiba Silicone Co.,  
10 Ltd., spherical crosslinked polysiloxane grain,  
av. grain size 0.9  $\mu$ m) 60 pts.wt.  
Methyl ethyl ketone 120 pts.wt.  
Cyclohexanone 120 pts.wt.  
(solid content 20%, solvent: methyl ethyl  
15 ketone/cyclohexanone = 1/1)

This mixture was dispersed by means of ultrasonic homogenizer "Sonifier 450 (manufactured by Branson)" for 2 hr while cooling with ice and stirring, thereby finishing spherical organic polymer grain  
20 dispersion c2.

(4) Preparation of coating liquid for 3rd layer

A coating liquid for 3rd layer was prepared by adding the following components to 542g of the aforementioned raw dispersion of sliding agent:

25 Diacetone alcohol 5950g  
Cyclohexanone 176g  
Ethyl acetate 1700g

Above Seahostar KEP50 dispersion (c1) 53.1g  
Above spherical organic polymer grain  
dispersion (c2) 300g  
FC431 (produced by 3M, solid content 50%, solvent:  
5 ethyl acetate) 2.65g  
BYK310 (produced by BYK ChemiJapan, solid  
content 25%) 5.3g.

The above 3rd-layer coating liquid was applied to  
the 2nd layer in a coating amount of 10.35 mL/m<sup>2</sup>, dried  
10 at 110°C and further postdried at 97°C for 3 min.

4) Application of light-sensitive layer by  
coating:

The thus obtained back layers on its side opposite  
to the support were coated with a plurality of layers  
15 of the following respective compositions, thereby  
obtaining a color negative film sample 101.

(Composition of light-sensitive layer)

The numeric value given beside the description of  
each component is for the coating amount expressed in  
20 the unit of g/m<sup>2</sup>. With respect to the silver halide  
and colloidal silver, the coating amount is in terms of  
silver quantity.

(Sample 101)

1st layer (1st antihalation layer)

25 Black colloidal silver silver 0.125  
Silver iodobromide emulsion grains having  
an average grain diameter of 0.07 μm

		silver	0.01
	Gelatin		0.922
	ExM-1		0.068
	ExC-1		0.002
5	ExC-3		0.002
	Cpd-2		0.001
	F-8		0.001
	HBS-1		0.050
	HBS-2		0.002
10	2nd layer (2nd antihalation layer)		
	Black colloidal silver	silver	0.052
	Gelatin		0.420
	ExF-1		0.002
	F-8		0.001
15	Solid disperse dye ExF-7		0.122
	HBS-1		0.076
	3rd layer (Interlayer)		
	ExC-2		0.050
	Cpd-1		0.090
20	Polyethylacrylate latex		0.200
	HBS-1		0.100
	Gelatin		0.700
	4th layer (Low-speed red-sensitive emulsion layer)		
	Em-D	silver	0.503
25	Em-C	silver	0.343
	ExC-1		0.190
	ExC-2		0.013

	ExC-3	0.070
	ExC-4	0.121
	ExC-5	0.010
	ExC-6	0.007
5	ExC-8	0.053
	ExC-9	0.020
	Cpd-2	0.025
	Cpd-4	0.025
	Cpd-7	0.015
10	UV-2	0.047
	UV-3	0.086
	UV-4	0.018
	HBS-1	0.240
	HBS-5	0.038
15	Gelatin	0.994

5th layer (Medium-speed red-sensitive emulsion layer)

	Em-B	silver	0.490
	Em-C	silver	0.455
	ExC-1		0.159
20	ExC-2		0.072
	ExC-3		0.020
	ExC-4		0.104
	ExC-5		0.023
	ExC-6		0.010
25	ExC-8		0.016
	ExC-9		0.005
	Cpd-2		0.036

	Cpd-4	0.028
	Cpd-7	0.020
	HBS-1	0.129
	Gelatin	0.890
5	6th layer (High-speed red-sensitive emulsion layer)	
	Em-A silver	1.110
	ExC-1	0.245
	ExC-3	0.035
	ExC-6	0.025
10	ExC-8	0.114
	ExC-9	0.022
	ExY-3	0.010
	Cpd-2	0.066
	Cpd-4	0.079
15	Cpd-7	0.030
	HBS-1	0.329
	HBS-2	0.120
	Gelatin	1.240
	7th layer (Interlayer)	
20	Cpd-1	0.094
	Cpd-6	0.369
	Solid disperse dye ExF-4	0.030
	HBS-1	0.049
	Polyethylacrylate latex	0.088
25	Gelatin	0.886
	8th layer (layer for donating interlayer effect to red-sensitive layer)	

	Em-J	silver	0.177
	Em-K	silver	0.170
	Cpd-4		0.034
	ExM-2		0.144
5	ExM-3		0.014
	ExY-1		0.018
	ExY-4		0.036
	ExC-7		0.026
	HBS-1		0.218
10	HBS-3		0.003
	HBS-5		0.030
	Gelatin		0.614
9th layer (Low-speed green-sensitive emulsion layer)			
	Em-H	silver	0.330
15	Em-G	silver	0.335
	Em-I	silver	0.082
	ExM-2		0.374
	ExM-3		0.045
	ExY-1		0.018
20	ExC-7		0.007
	HBS-1		0.098
	HBS-3		0.010
	HBS-4		0.074
	HBS-5		0.544
25	Cpd-5		0.010
	Cpd-7		0.020
	Gelatin		1.465

10th layer (Medium-speed green-sensitive emulsion layer)

	Em-F	silver	0.459
	ExM-2		0.057
5	ExM-3		0.028
	ExY-3		0.008
	ExC-6		0.010
	ExC-7		0.011
	ExC-8		0.010
10	HBS-1		0.064
	HBS-3		0.002
	HBS-4		0.020
	HBS-5		0.020
	Cpd-5		0.004
15	Cpd-7		0.010
	Gelatin		0.443

11th layer (High-speed green-sensitive emulsion layer)

	Em-E	silver	0.788
	ExC-6		0.002
20	ExC-8		0.012
	ExM-1		0.014
	ExM-2		0.033
	ExM-3		0.033
	ExY-3		0.007
25	Cpd-3		0.004
	Cpd-4		0.007
	Cpd-5		0.010

	Cpd-7		0.020
	HBS-1		0.144
	HBS-3		0.003
	HBS-4		0.020
5	HBS-5		0.037
	Polyethylacrylate latex		0.099
	Gelatin		0.930
	12th layer (Yellow filter layer)		
	Cpd-1		0.098
10	Solid disperse dye ExF-2		0.070
	Solid disperse dye ExF-5		0.010
	Oil-soluble dye ExF-6		0.010
	HBS-1		0.049
	Gelatin		0.626
15	13th layer (Low-speed blue-sensitive emulsion layer)		
	Em-O	silver	0.108
	Em-M	silver	0.324
	Em-N	silver	0.242
	ExC-1		0.022
20	ExC-7		0.015
	ExY-1		0.002
	ExY-2		0.895
	ExY-4		0.056
	Cpd-2		0.102
25	Cpd-3		0.004
	HBS-1		0.225
	HBS-5		0.070



	Gelatin	1.550
	14th layer (High-speed blue-sensitive emulsion layer)	
	Em-L	silver 0.720
	ExY-2	0.205
5	ExY-3	0.008
	ExY-4	0.070
	Cpd-2	0.074
	Cpd-3	0.001
	Cpd-7	0.030
10	HBS-1	0.120
	Gelatin	0.680
	15th layer (1st protective layer)	
	Silver iodobromide emulsion grains having an average grain diameter of $0.07\mu\text{m}$	
15		silver 0.305
	UV-1	0.211
	UV-2	0.132
	UV-3	0.198
	UV-4	0.026
20	F-11	0.009
	S-1	0.086
	HBS-1	0.175
	HBS-4	0.050
	Gelatin	1.986
25	16th layer (2nd protective layer)	
	H-1	0.400
	B-1 (diameter $1.7\mu\text{m}$ )	0.050

B-2 (diameter 1.7 $\mu$ m)	0.150
B-3	0.050
S-1	0.200
Gelatin	0.750

5           In addition to the above components, W-1 to W-6,  
B-4 to B-6, F-1 to F-19, a lead salt, a platinum salt,  
an iridium salt and a rhodium salt were appropriately  
added to the individual layers in order to improve the  
storability, processability, resistance to pressure,  
10   mildewproofing and antiseptic properties, antistatic  
properties and coating property thereof.

Preparation of dispersion of organic solid disperse  
dye:

15           The ExF-2 of the 12th layer was dispersed by the  
following method. Specifically,

Wet cake of ExF-2 (containing 17.6 wt.% water)	2.800 kg
Sodium octylphenyldiethoxymethanesulfonate (31 wt.% aq. solution)	0.376 kg
20   F-15 (7% aq. solution)	0.011 kg
Water	4.020 kg
Total	7.210 kg

(adjusted to pH = 7.2 with NaOH).

25           Slurry of the above composition was agitated by  
means of a dissolver, and further dispersed by means of  
agitator mill LMK-4 under such conditions that the  
peripheral speed, delivery rate and packing ratio of

0.3 mm-diameter zirconia beads were 10 m/s, 0.6 kg/min and 80%, respectively, until the absorbance ratio of the dispersion became 0.29. Thus, a solid particulate dispersion was obtained, wherein the average particle diameter of dye particulate was 0.29  $\mu\text{m}$ .

Solid dispersions of ExF-4 and ExF-7 were obtained in the same manner. The average particle diameters of these dye particulates were 0.28  $\mu\text{m}$  and 0.49  $\mu\text{m}$ , respectively. ExF-5 was dispersed by the microprecipitation dispersion method described in Example 1 of EP. No. 549,489A. The average particle diameter thereof was 0.06  $\mu\text{m}$ .

Table 1

Emulsion	Average iodide (mol%)	Equivalent sphere diameter ( $\mu\text{m}$ )	Aspect ratio	Equivalent circle diameter ( $\mu\text{m}$ )	Grain thickness ( $\mu\text{m}$ )	Shape
Em-A	4	0.92	14	2	0.14	Tabular
Em-B	5	0.8	12	1.6	0.13	Tabular
Em-C	4.7	0.51	7	0.85	0.12	Tabular
Em-D	3.9	0.37	2.7	0.4	0.15	Tabular
Em-E	5	0.92	14	2	0.14	Tabular
Em-F	5.5	0.8	12	1.6	0.13	Tabular
Em-G	4.7	0.51	7	0.85	0.12	Tabular
Em-H	3.7	0.49	3.2	0.58	0.18	Tabular
Em-I	2.8	0.29	1.2	0.27	0.23	Tabular
Em-J	5	0.8	12	1.6	0.13	Tabular
Em-K	3.7	0.47	3	0.53	0.18	Tabular
Em-L	5.5	1.4	9.8	2.6	0.27	Tabular
Em-M	8.8	0.64	5.2	0.85	0.16	Tabular
Em-N	3.7	0.37	4.6	0.55	0.12	Tabular
Em-O	1.8	0.19	—	—	—	Cubic

The silver halide grains contained in emulsions Em-A to -O are all grains of silver iodobromide.

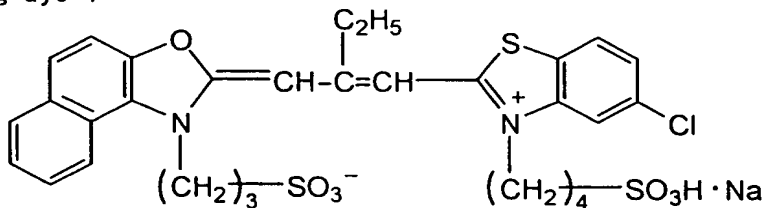
In Table 1, emulsions Em-A to -C contained the optimum amount of spectral sensitizing dyes 1 to 3, and  
5 were subjected to gold sensitization, sulfur sensitization and selenium sensitization optimally. Emulsions Em-E to -G contained the optimum amount of spectral sensitizing dyes 4 to 6, and were subjected to gold sensitization, sulfur sensitization and selenium sensitization optimally.  
10 Emulsion Em-J contained the optimum amount of spectral sensitizing dyes 7 and 8, and was subjected to gold sensitization, sulfur sensitization and selenium sensitization optimally. Emulsion Em-L contained the optimum amount of spectral sensitizing dyes 9 to 11, and was subjected to gold sensitization, sulfur sensitization and selenium sensitization optimally.  
15 Emulsion Em-O contained the optimum amount of spectral sensitizing dyes 10 to 12, and was subjected to gold sensitization and sulfur sensitization optimally. Emulsions Em-D, -H, -I, -K, -M and -N contained the optimum amount of spectral sensitizing dye listed in Table 2, and were subjected to gold sensitization, sulfur sensitization and selenium sensitization optimally.  
20

Table 2

Emulsion	Sensitizing dye	Addition amount (mo/mol Ag)
Em-D	Sensitizing dye 1	$5.44 \times 10^{-4}$
	Sensitizing dye 2	$2.35 \times 10^{-4}$
	Sensitizing dye 3	$7.26 \times 10^{-6}$
Em-H	Sensitizing dye 8	$6.52 \times 10^{-4}$
	Sensitizing dye 13	$1.35 \times 10^{-4}$
	Sensitizing dye 6	$2.48 \times 10^{-5}$
Em-I	Sensitizing dye 8	$6.09 \times 10^{-4}$
	Sensitizing dye 13	$1.26 \times 10^{-4}$
	Sensitizing dye 6	$2.32 \times 10^{-5}$
Em-K	Sensitizing dye 7	$6.27 \times 10^{-4}$
	Sensitizing dye 8	$2.24 \times 10^{-4}$
Em-M	Sensitizing dye 9	$2.43 \times 10^{-4}$
	Sensitizing dye 10	$2.43 \times 10^{-4}$
	Sensitizing dye 11	$2.43 \times 10^{-4}$
Em-N	Sensitizing dye 9	$3.28 \times 10^{-4}$
	Sensitizing dye 10	$3.28 \times 10^{-4}$
	Sensitizing dye 11	$3.28 \times 10^{-4}$

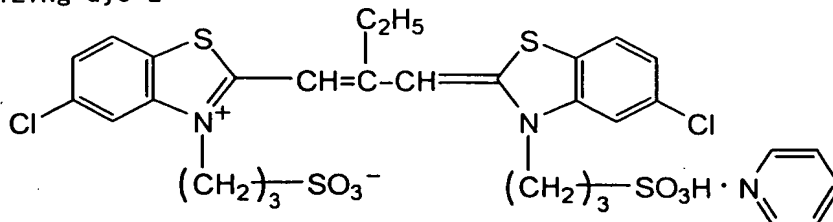
The sensitizing dyes used in the examples of the present invention will be listed below.

Sensitizing dye 1

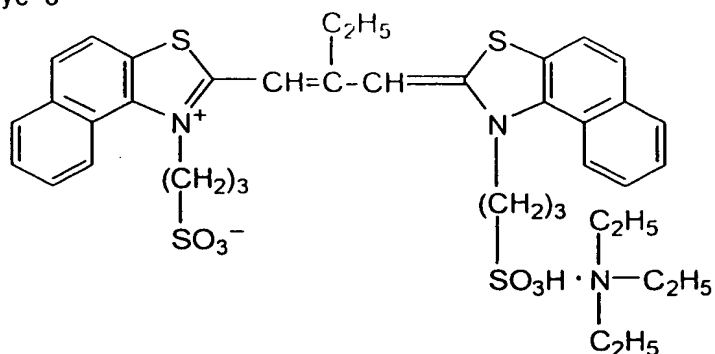


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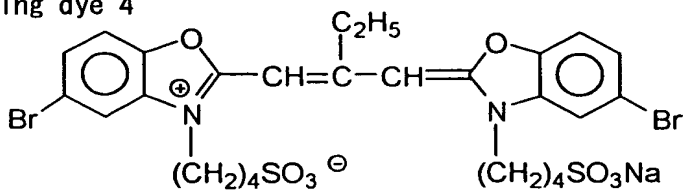
Sensitizing dye 2



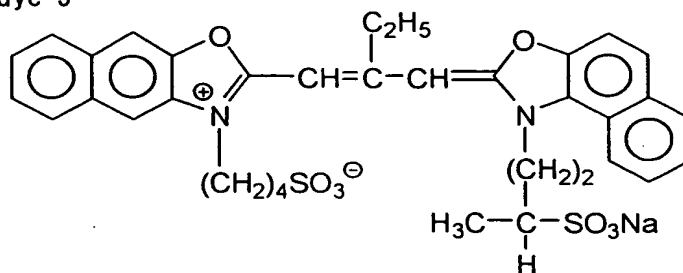
Sensitizing dye 3



Sensitizing dye 4

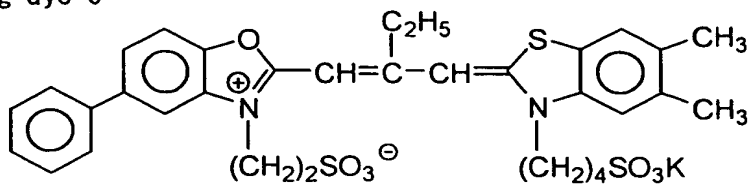


Sensitizing dye 5

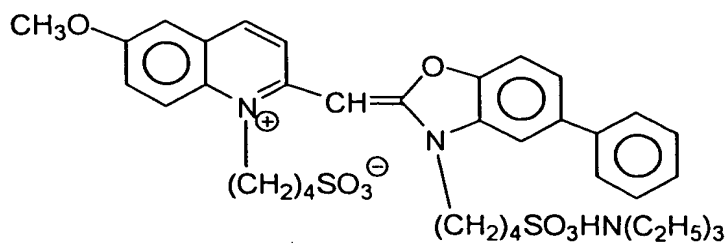


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Sensitizing dye 6

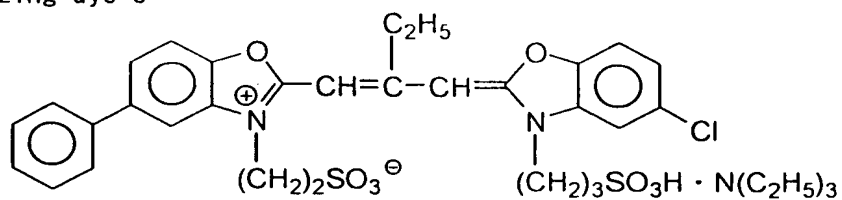


Sensitizing dye 7

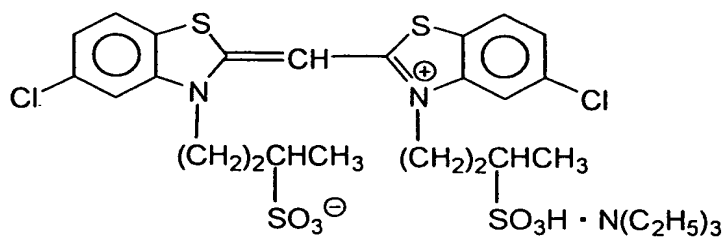


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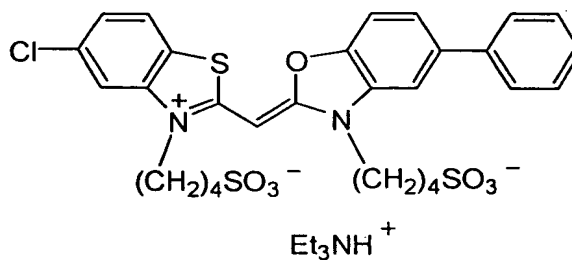
Sensitizing dye 8



Sensitizing dye 9

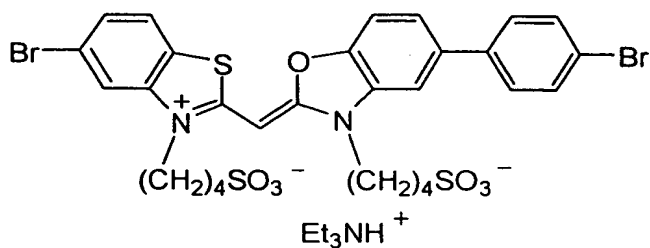


Sensitizing dye 10

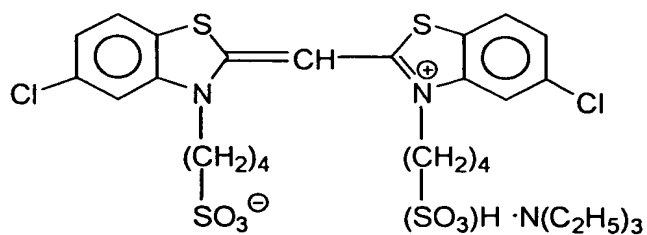


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Sensitizing dye 11

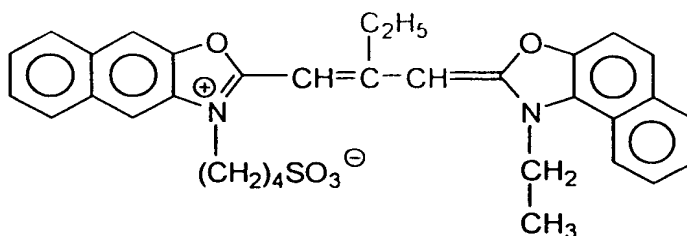


Sensitizing dye 12

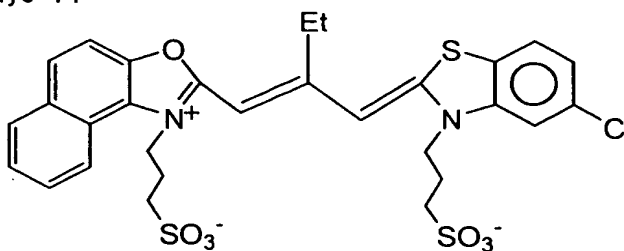




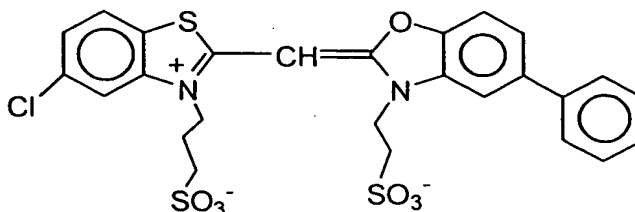
Sensitizing dye 13



Sensitizing dye 14

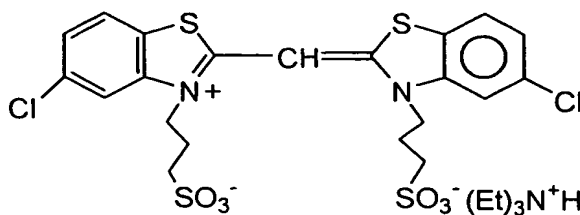


Sensitizing dye 15



5

Sensitizing dye 16



10

For the preparation of the tabular grains, a low-molecular-weight gelatin was used according to the examples described in JP-A-1-158426.

Emulsions Em-A to -K contained the optimum amount of Ir and Fe.

Emulsions Em-L to -O were reduction-sensitized at the time of preparing the grains.

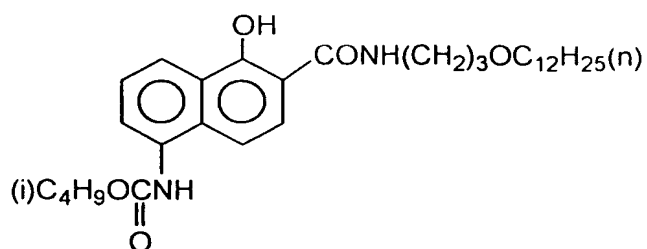
If a high-voltage electron microscope is used, it is observed that the tabular grains have dislocation lines as described in the publication of JP-A-3-237450.

5 With respect to Emulsions Em-A to -C and -J, dislocation introduction was performed by using the iodide ion-releasing agent according to the examples described in the publication of JP-A-6-11782.

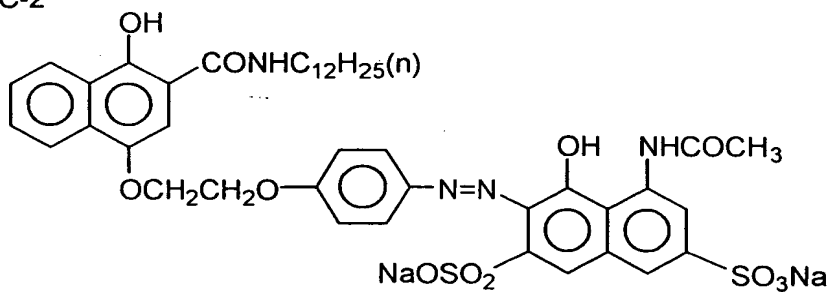
10 With respect to emulsion Em-E, dislocation introduction was performed by using the silver iodide fine grains prepared immediately before being added. The preparation was conducted in a different chamber having a magnetic coupling induction type mixer described in the publication of JP-A-10-43570.

15 The other compounds used in the examples of the present invention will be listed below.

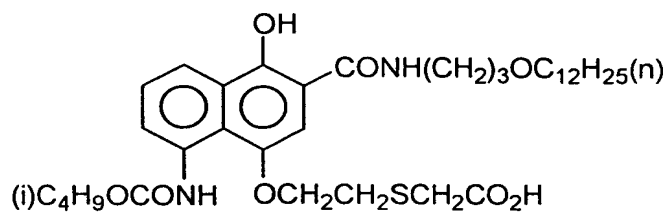
ExC-1



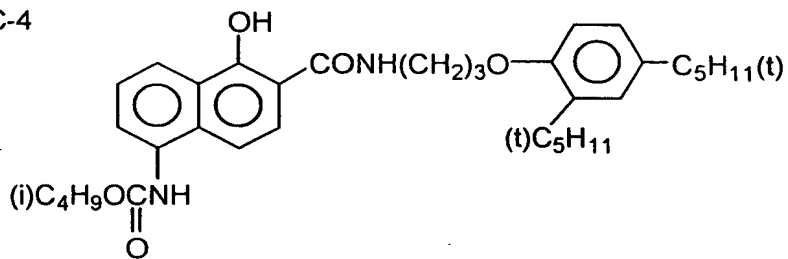
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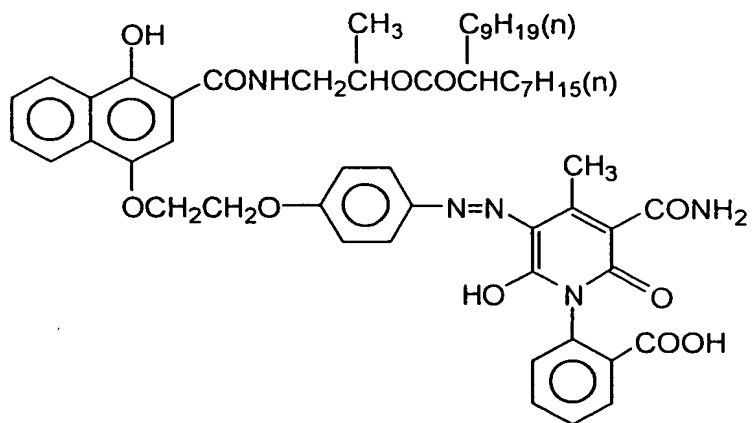
ExC-3



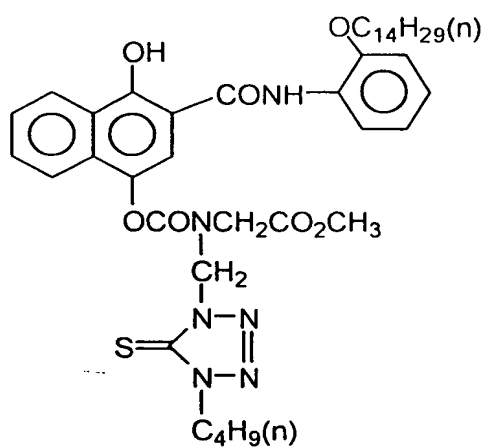
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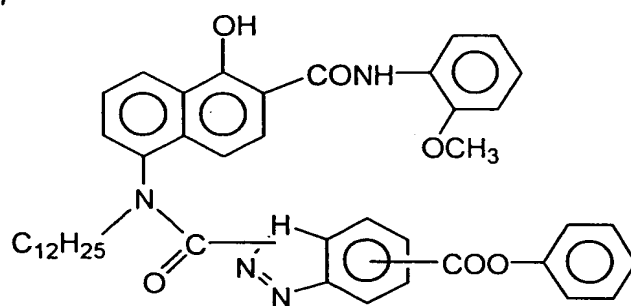
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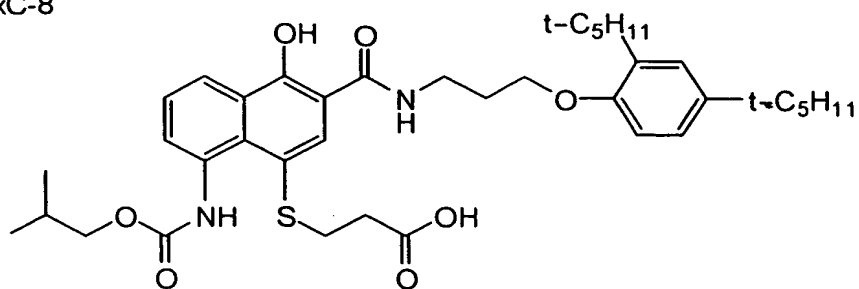
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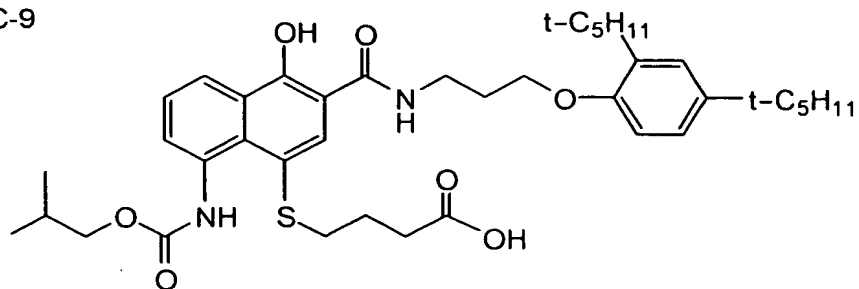
ExC-7



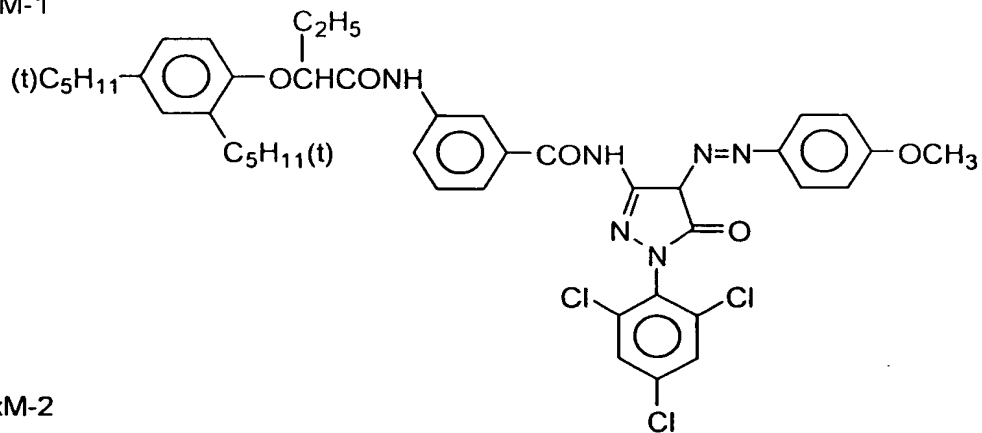
ExC-8



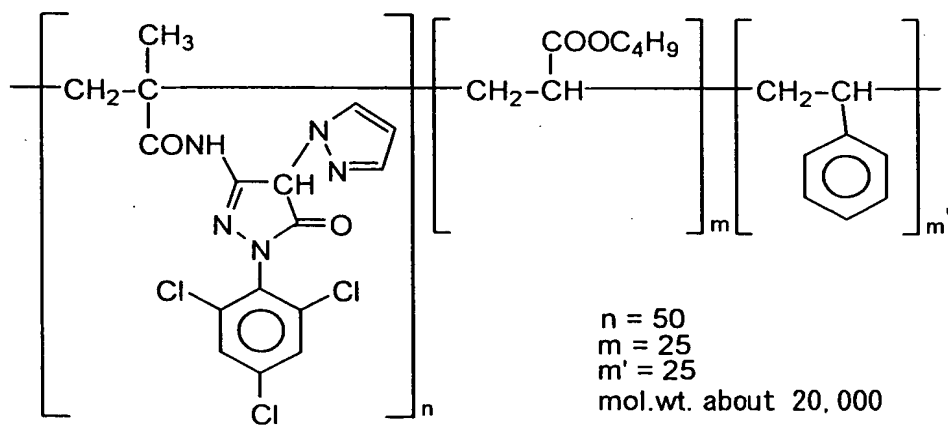
ExC-9



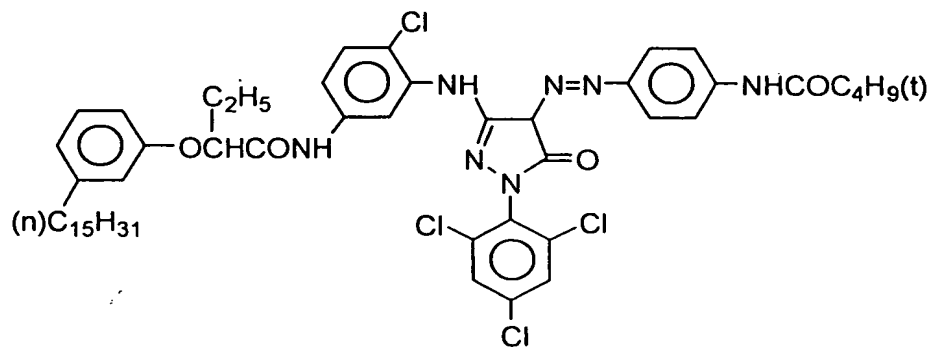
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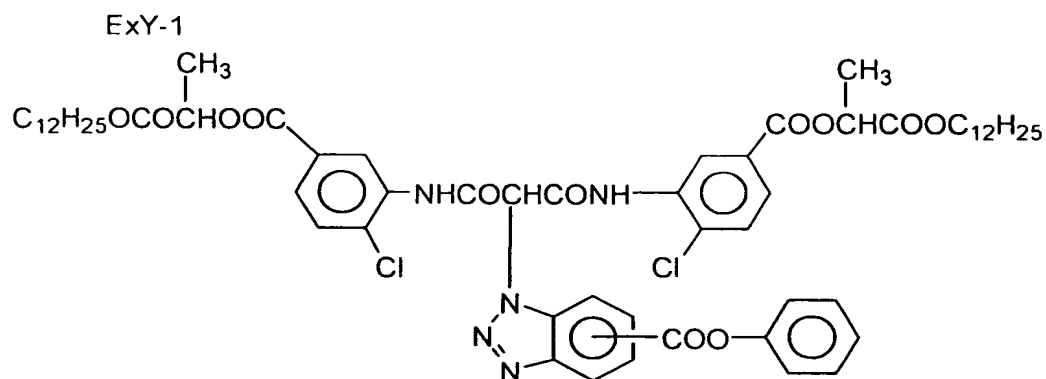


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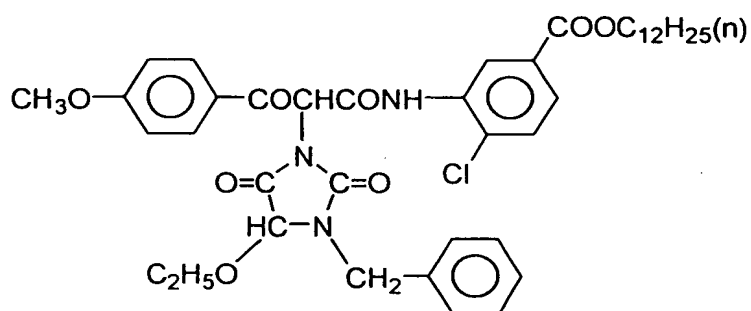


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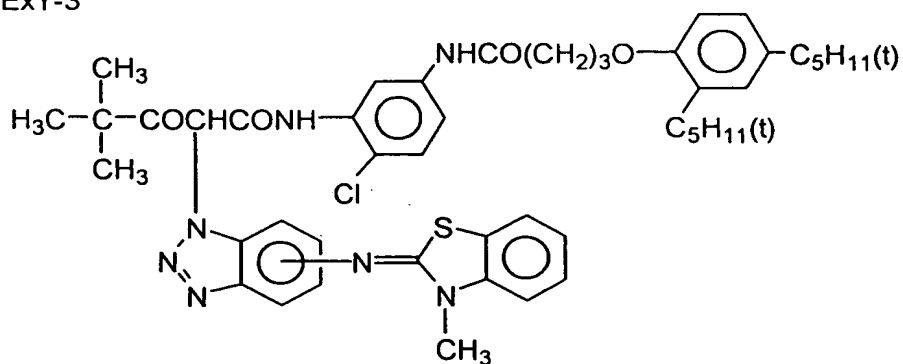




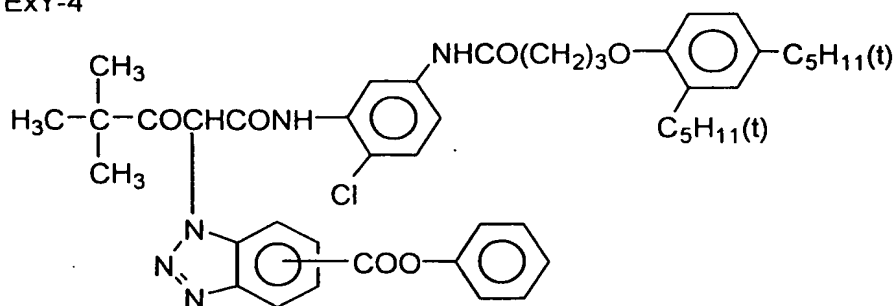
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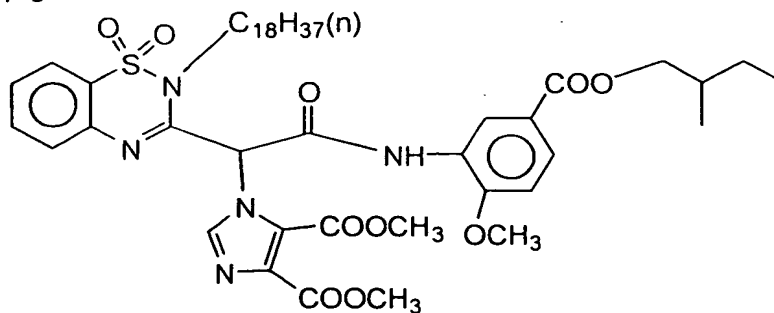
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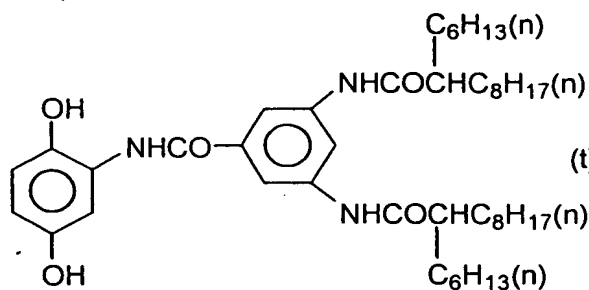
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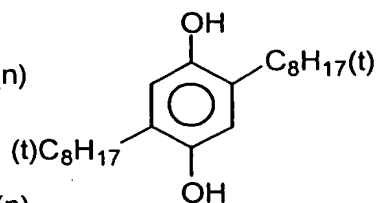
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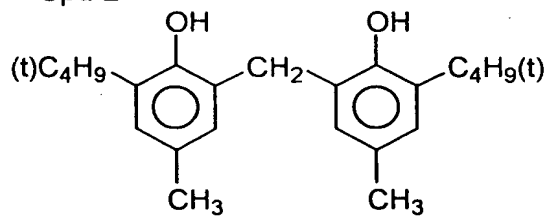
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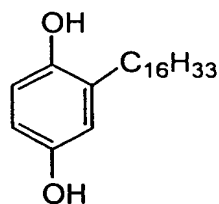
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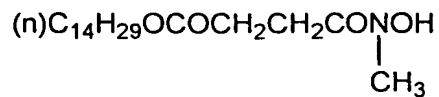
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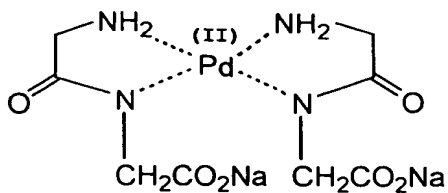
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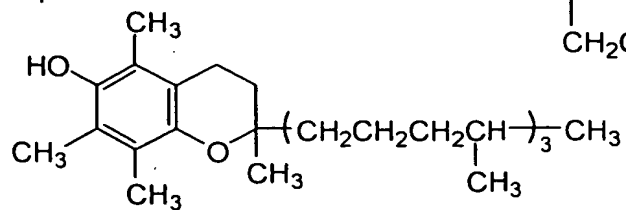
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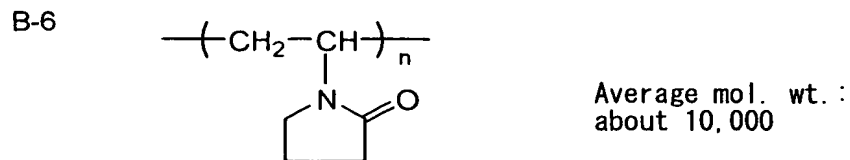
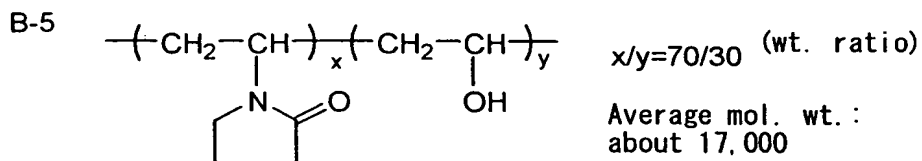
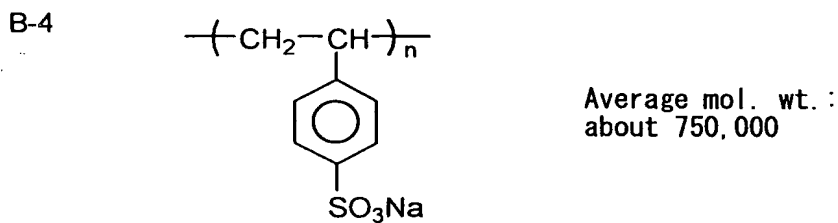
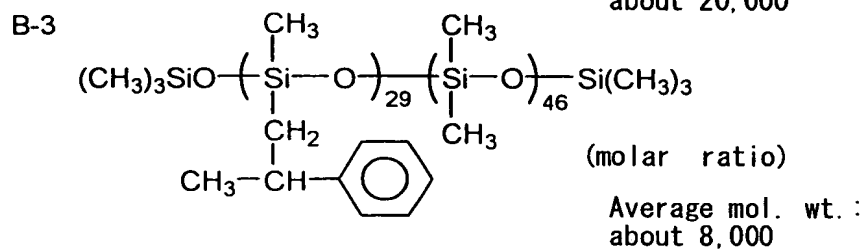
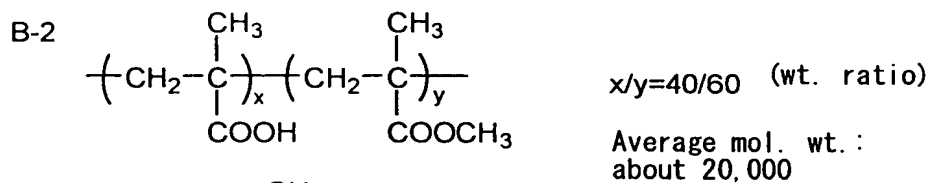
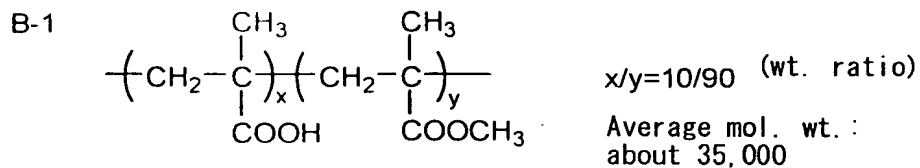


Cpd-6



Cpd-7

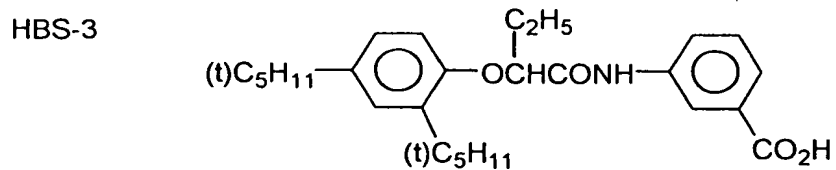






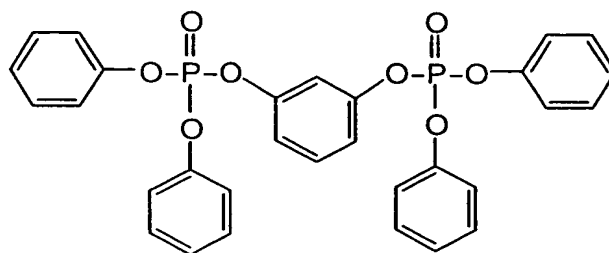
HBS-1 Tricresyl phosphate

HBS-2 Di-n-butyl phthalate

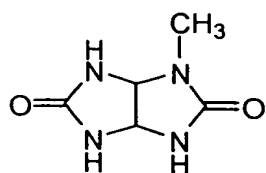


HBS-4 Tri (2-ethylhexyl) phosphate

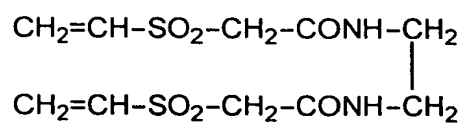
HBS-5



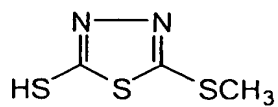
S-1



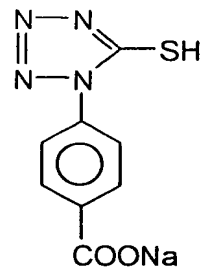
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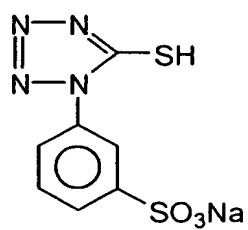
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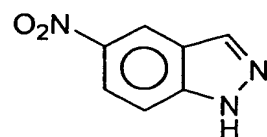
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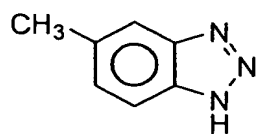
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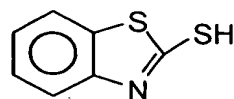
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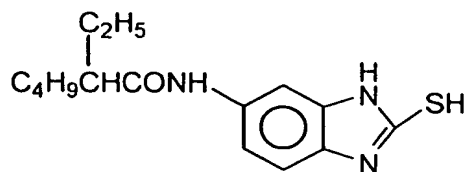
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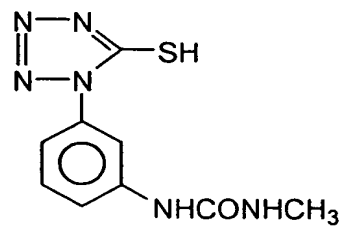
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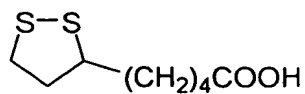
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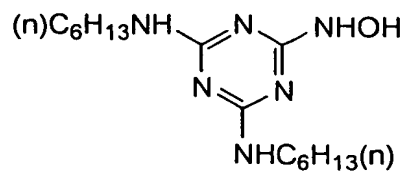
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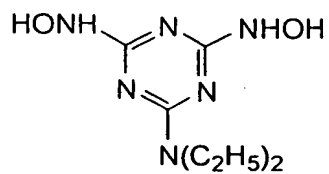
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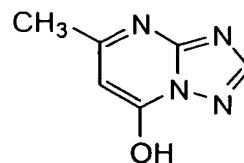
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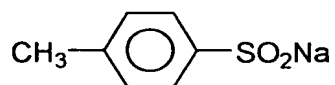
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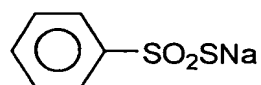
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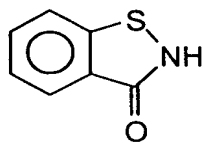
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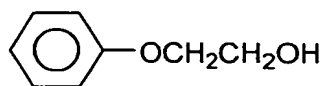
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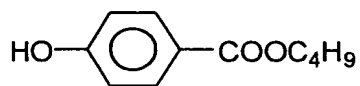
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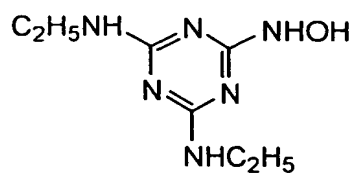
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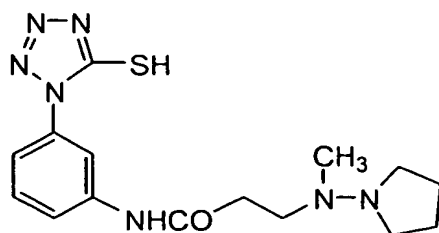
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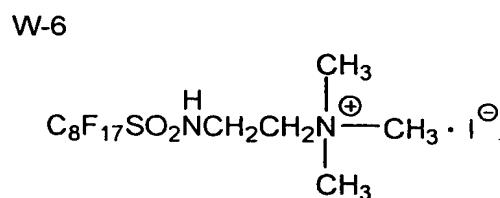
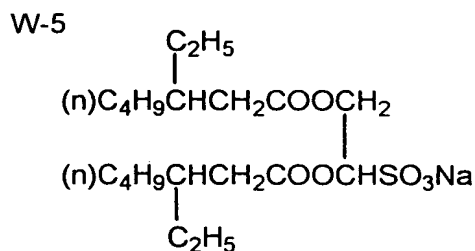
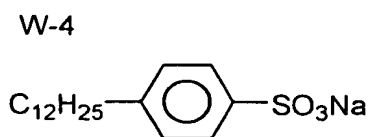
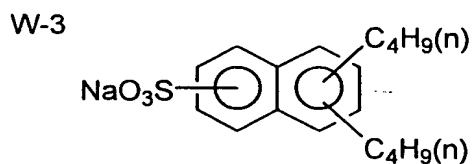
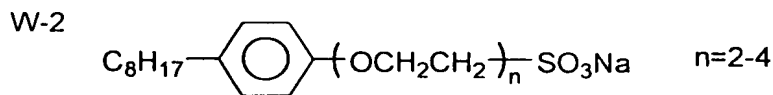
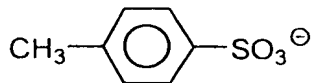
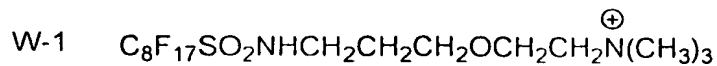


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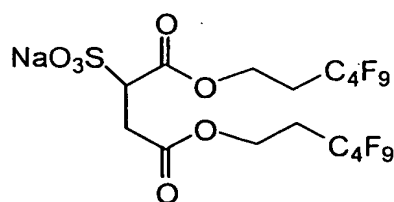


F-19

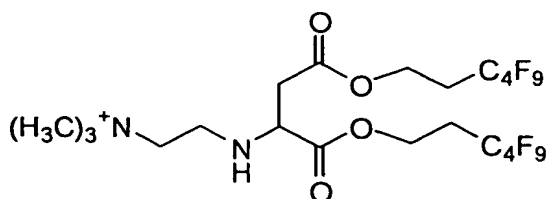




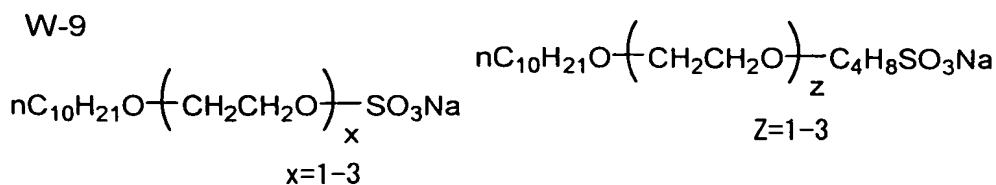
W-7



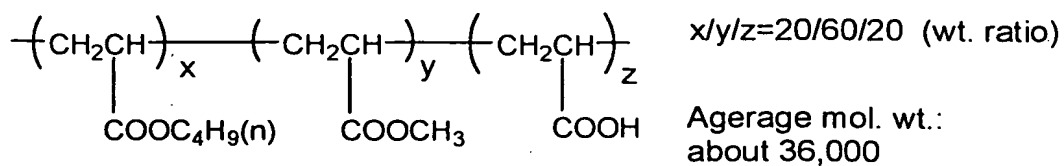
W-8

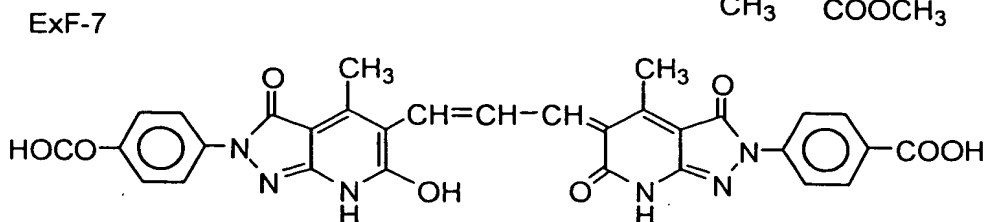
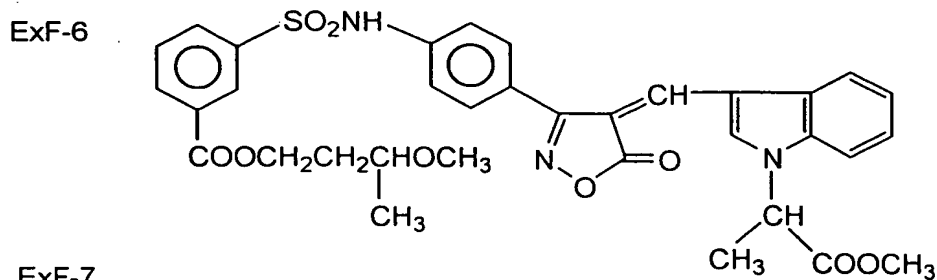
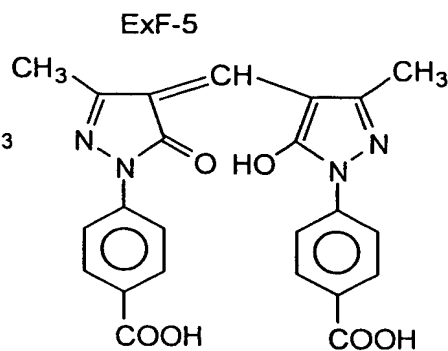
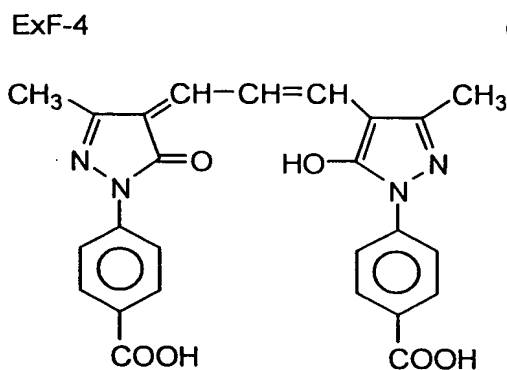
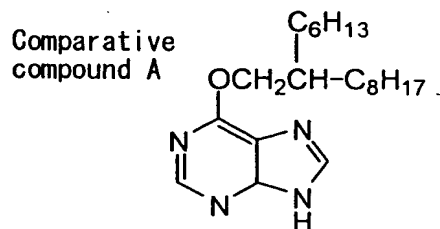
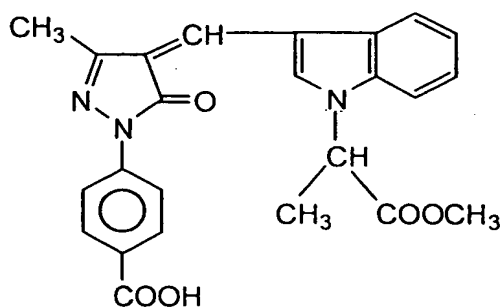
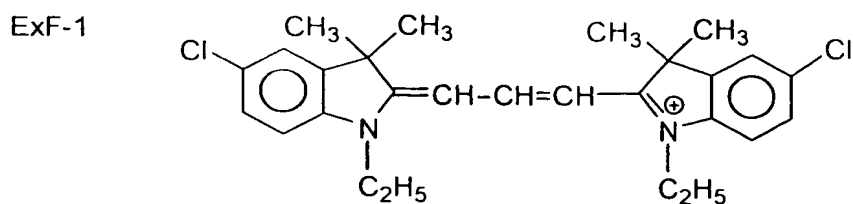


W-10



W-11





The above silver halide color photosensitive material is regarded as sample 101.

(Preparation of Samples 102 to 119)

Samples 102 to 119 were prepared in the same manner as sample 101, except that the compound of general formula (M) or (C) of the present invention was added to the 6th, 11th, and 14th layers of sample 101, as shown in Table 3.

Samples 101 to 119 were exposed for 1/100 second through a gelatin filter SC-39 manufactured by Fuji Photo Film Co., Ltd. and a continuous wedge.

Each of the exposed samples was processed by the following method.

(Processing steps)

	Step	Time	Temp.
	Color development	3 min 15 sec	38°C
15	Bleaching	3 min 00 sec	38°C
	Washing	30 sec	24°C
	Fixing	3 min 00 sec	38°C
	Washing (1)	30 sec	24°C
	Washing (2)	30 sec	24°C
20	Stabilization	30 sec	38°C
	Drying	4 min 20 sec	55°C

The composition of each processing solution was as follows.

(Color developer)

(unit: g)

25	Diethylenetriaminepentaacetic acid	1.0
	1-Hydroxyethylidene-1,1-diphosphonic acid	2.0
	Sodium sulfite	4.0

	Potassium carbonate	30.0
	Potassium bromide	1.4
	Potassium iodide	
	1.5 mg	
5	Hydroxylamine sulfate	2.4
	4-[N-ethyl-N-( $\beta$ -hydroxyethyl)amino]-2-methylaniline sulfate	4.5
	Water to make	1.0 L
	pH (adjusted by potassium hydroxide and sulfuric acid)	10.05
10	(Bleach-fix soln.)	(unit: g)
	Fe(III) sodium ethylenediaminetetraacetate trihydrate	100.0
	Disodium ethylenediaminetetraacetate	10.0
15	3-Mercapto-1,2,4-triazole	0.03
	Ammonium bromide	140.0
	Ammonium nitrate	30.0
	Aq. ammonia (27%)	6.5 ml
	Water to make	1.0 L
20	pH (adjusted by aqueous ammonia and nitric acid)	6.0
	(Fixing solution)	(unit: g)
	Disodium ethylenediaminetetraacetate	0.5
	Sodium sulfite	20.0
25	Aq. soln. of ammonium thiosulphate (700 g/L)	295.0 ml
	Acetic acid (90%)	3.3

	Water to make	1.0 L
	pH (adjusted by aqueous ammonia and nitric acid)	6.7
	(Stabilizer solution)	(unit: g)
5	p-Nonylphenoxypolyglycidol (glycidol av. polymerization degree: 10)	0.2
	Ethylenediaminetetraacetic acid	0.05
	1,2,4-Triazole	1.3
	1,4-Bis(1,2,4-triazol-1-ylmethyl)piperazine	0.75
10	Hydroxyacetic acid	0.02
	Hydroxyethylcellulose (HEC SP-2000 produced by Daicel Chemical Industries, Ltd.)	0.1
	1,2-Benzisothiazolin-3-one	0.05
	Water to make	1.0 L
15	pH	8.5.

The speeds of the red-sensitive layer, green-sensitive layer and blue-sensitive layer were indicated with the logarithmic value of the reciprocal of the exposure amount necessary to give the cyan, magenta, and yellow color image densities of the minimum density plus 0.2, respectively, and represented by the difference with respect to the sample 101.

With respect to the graininess, the RMS granularity of the cyan, magenta, and yellow color images at the fog density plus 0.2 was determined and evaluated. The graininess was indicated with the relative value where the graininess of sample 101 is



assumed as 100.

In order to evaluate the substantial speed  
increase, if the RMS granularity varied with the  
increase of speed, the amounts of ExY-3 in the sixth,  
5 eleventh, and fourteenth layers were adjusted, thereby  
matching the RMS granularity with that of Sample 101.  
The speed was then compared.

Table 3

Sample No.	Compound of general formula (M) or general formula (C)				Addition amount (per mol of Ag $\times 10^{-3}$ mol)			Speed			Graininess		
	No.	pKa	$\Delta pAgF$	CRV	6th layer	11th layer	14th layer	R layer	G layer	B layer	R layer	G layer	B layer
101 (Comp.)	—	—	—	—	—	—	—	0.00	0.00	0.00	100	100	100
102 (Comp.)	Comp. comp. A	—	—	—	10	10	10	+0.03	+0.03	+0.03	102	102	102
103 (Inv.)	(64)	8.83	0.46	0.14	10	10	10	+0.06	+0.05	+0.06	100	101	101
104 (Inv.)	(70)	8.73	0.45	0.14	10	10	10	+0.06	+0.05	+0.06	100	101	101
105 (Inv.)	(55)	8.43	0.44	0.14	10	10	10	+0.08	+0.06	+0.07	100	101	101
106 (Inv.)	(56)	8.48	0.35	0.18	10	10	10	+0.08	+0.05	+0.07	102	100	101
107 (Inv.)	(57)	8.51	0.20	0.14	10	10	10	+0.10	+0.07	+0.08	102	102	101
108 (Inv.)	(2)	8.12	0.21	0.16	10	10	10	+0.13	+0.10	+0.13	101	101	101
109 (Inv.)	(3)	8.13	0.20	0.16	10	10	10	+0.13	+0.09	+0.12	102	100	102
110 (Inv.)	(9)	8.15	0.22	0.13	10	10	10	+0.13	+0.09	+0.11	102	102	102
111 (Inv.)	(17)	8.13	0.18	0.16	10	10	10	+0.15	+0.12	+0.14	102	101	102
112 (Inv.)	(20)	6.49	0.20	0.17	10	10	10	+0.14	+0.12	+0.13	101	101	101
113 (Inv.)	(58)	8.25	0.20	0.02	10	10	10	+0.17	+0.14	+0.16	101	101	101
114 (Inv.)	(15)	8.13	0.20	0.03	10	10	10	+0.17	+0.14	+0.16	101	101	102
115 (Inv.)	(18)	8.14	0.20	0.03	10	10	10	+0.17	+0.14	+0.16	102	102	102
116 (Inv.)	(59)	8.14	0.21	0.03	10	10	10	+0.18	+0.15	+0.17	102	102	102
117 (Inv.)	(2)	8.12	0.21	0.16	10	—	—	+0.13	0.00	0.00	101	101	101
118 (Inv.)	(2)	8.12	0.21	0.16	—	10	—	0.00	+0.10	0.00	101	101	101
119 (Inv.)	(2)	8.12	0.21	0.16	—	—	10	0.00	0.00	+0.13	101	101	101

Note: R layer = Red-sensitive layer; G layer = Blue-sensitive layer; B layer = Blue-sensitive layer

Comp. comp. A = Comparative compound A

As described above, it is apparent that the method of the present invention is excellent in obtaining a high quality image. This is made possible by increasing the speed of the photosensitive material without deteriorating the graininess.

It is also apparent from samples 117 to 119 that the effect of the speed increase is more pronounced if the compound represented by formula (M) is used for the red-sensitive layer and blue-sensitive layer, than used for the green-sensitive layer.

#### Example 2

Sample 201 was prepared in the same manner as sample 106, except that the compound (56) used for the eleventh layer of sample 106 described in Example 1 was moved to the twelfth layer.

Sample 201 was evaluated in the same manner as sample 106 using the method described in Example 1. The speed increase effect of the green-sensitive layer was 0.03, which was reduced with respect to 0.06 of sample 106. However, as the coating liquid of the eleventh and twelfth layers was left over 12 hours at 40 °C before preparation of sample 201, a fog increase did not occur in sample 201, thus making sample 201 advantageous over the undesired fog increase occurring in the eleventh layer of sample 106.

It is preferable that the compound of the present invention be added directly to the light-sensitive

layer, from the viewpoint of increasing the effect. However, from the viewpoint of preventing the above side effects, it has been found preferable that the compound be added to the adjacent nonsensitive layer.

5 Example 3

The support used in Example 3 was prepared using the same method as Example 1.

Application of Light-Sensitive Layer by Coating

10 Next, the thus obtained back layers on its side opposite to the support were coated with a plurality of layers of the following compositions, thereby obtaining a color negative film sample 301.

(Composition of Light-Sensitive Layer)

15 The numeric value given beside the description of each component indicates the coating amount represented in the unit of  $\text{g/m}^2$ . With respect to the silver halide, the coating amount is indicated in terms of silver quantity.

20 For each specific compound, numeral is used in common with Example 1.

(Sample 301)

1st layer (1st antihalation layer)

Black colloidal silver	silver	0.104
Silver iodobromide emulsion grains having		
25 an average grain diameter of $0.07\mu\text{m}$		
	silver	0.011
Gelatin		0.910

	ExM-1	0.060
	ExC-1	0.002
	ExC-3	0.002
	Cpd-2	0.001
5	F-8	0.001
	HBS-1	0.050
	HBS-2	0.002
	2nd layer (2nd antihalation layer)	
	Black colloidal silver	silver 0.055
10	Gelatin	0.413
	ExF-1	0.002
	F-8	0.001
	Solid disperse dye ExF-7	0.120
	HBS-1	0.076
15	3rd layer (Interlayer)	
	ExC-2	0.050
	Cpd-1	0.090
	Polyethylacrylate latex	0.200
	HBS-1	0.100
20	Gelatin	0.700
	4th layer (Low-speed red-sensitive emulsion layer)	
	Em-C'	silver 0.515
	Em-D'	silver 0.344
	ExC-1	0.193
25	ExC-2	0.010
	ExC-3	0.073
	ExC-4	0.120

	ExC-5	0.010
	ExC-6	0.007
	ExC-8	0.053
	ExC-9	0.020
5	Cpd-2	0.020
	Cpd-4	0.025
	Cpd-7	0.015
	UV-2	0.047
	UV-3	0.086
10	UV-4	0.018
	HBS-1	0.240
	HBS-5	0.038
	Gelatin	0.994
5th layer (Medium-speed red-sensitive emulsion layer)		
15	Em-B'	silver 0.943
	ExC-1	0.145
	ExC-2	0.076
	ExC-3	0.023
	ExC-4	0.100
20	ExC-5	0.023
	ExC-6	0.010
	ExC-8	0.016
	ExC-9	0.005
	Cpd-2	0.036
25	Cpd-4	0.028
	Cpd-7	0.020
	HBS-1	0.120

	Gelatin		0.894
	6th layer (High-speed red-sensitive emulsion layer)		
	Em-A'	silver	1.230
	ExC-1		0.230
5	ExC-3		0.034
	ExC-6		0.025
	ExC-8		0.112
	ExC-9		0.023
	ExY-3		0.011
10	Cpd-2		0.062
	Cpd-4		0.079
	Cpd-7		0.030
	HBS-1		0.329
	HBS-2		0.120
15	Gelatin		1.300
	7th layer (Interlayer)		
	Cpd-1		0.094
	Cpd-6		0.369
	Solid disperse dye ExF-4		0.030
20	HBS-1		0.049
	Polyethylacrylate latex		0.088
	Gelatin		0.886
	8th layer (layer for donating interlayer effect to red-sensitive layer)		
25	Em-E'	silver	0.343
	Cpd-4		0.033
	ExM-2		0.143

	ExM-3		0.014
	ExY-1		0.015
	ExY-4		0.039
	ExC-7		0.022
5	HBS-1		0.218
	HBS-3		0.003
	HBS-5		0.030
	Gelatin		0.614
9th layer (Low-speed green-sensitive emulsion layer)			
10	Em-I'	silver	0.323
	Em-J'	silver	0.345
	Em-H'	silver	0.082
	ExM-2		0.374
	ExM-3		0.044
15	ExY-1		0.013
	ExC-7		0.007
	HBS-1		0.098
	HBS-3		0.010
	HBS-4		0.074
20	HBS-5		0.544
	Cpd-5		0.010
	Cpd-7		0.020
	Gelatin		1.464
10th layer (Medium-speed green-sensitive emulsion layer)			
25	Em-G'	silver	0.459
	ExM-2		0.060



	ExM-3	0.026
	ExY-3	0.005
	ExC-6	0.013
	ExC-7	0.011
5	ExC-8	0.010
	HBS-1	0.064
	HBS-3	0.002
	HBS-4	0.020
	HBS-5	0.020
10	Cpd-5	0.004
	Cpd-7	0.010
	Gelatin	0.432
11th layer (High-speed green-sensitive emulsion layer)		
	Em-F'	silver 0.880
15	Em-H'	silver 0.110
	ExC-6	0.003
	ExC-8	0.012
	ExM-1	0.016
	ExM-2	0.034
20	ExM-3	0.032
	ExY-3	0.007
	Cpd-3	0.004
	Cpd-4	0.007
	Cpd-5	0.010
25	Cpd-7	0.020
	HBS-1	0.144
	HBS-3	0.003

	HBS-4		0.020
	HBS-5		0.037
	Polyethylacrylate latex		0.099
	Gelatin		0.988
5	12th layer (Yellow filter layer)		
	Cpd-1		0.098
	Solid disperse dye ExF-2		0.070
	Solid disperse dye ExF-5		0.010
	Oil-soluble dye ExF-6		0.010
10	HBS-1		0.049
	Gelatin		0.626
	13th layer (Low-speed blue-sensitive emulsion layer)		
	Em-O'	silver	0.123
	Em-M'	silver	0.309
15	Em-N'	silver	0.211
	ExC-1		0.020
	ExC-7		0.015
	ExY-1		0.002
	ExY-2		0.355
20	ExY-4		0.056
	ExY-5		0.410
	Cpd-2		0.102
	Cpd-3		0.004
	HBS-1		0.225
25	HBS-5		0.070
	Gelatin		1.450
	14th layer (High-speed blue-sensitive emulsion layer)		

	Em-K'	silver	0.810
	Em-L'		0.100
	ExY-2		0.080
	ExY-3		0.005
5	ExY-4		0.073
	ExY-5		0.101
	Cpd-2		0.074
	Cpd-3		0.001
	Cpd-7		0.030
10	HBS-1		0.124
	Gelatin		0.699

15th layer (1st protective layer)

Silver iodobromide emulsion grains having  
an average grain diameter of  $0.07\mu\text{m}$

15		silver	0.305
	UV-1		0.211
	UV-2		0.132
	UV-3		0.198
	UV-4		0.026
20	UV-5		0.200
	F-11		0.009
	S-1		0.086
	HBS-1		0.175
	HBS-4		0.050
25	Gelatin		2.120

16th layer (2nd protective layer)

	H-1		0.400
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	B-1 (diameter 1.7 $\mu$ m)	0.050
	B-2 (diameter 1.7 $\mu$ m)	0.150
	B-3	0.050
	S-1	0.200
5	Gelatin	0.750

In addition to the above components, W-1 to W-11, B-4 to B-6, F-1 to F-19, a lead salt, a platinum salt, an iridium salt and a rhodium salt were appropriately added to the individual layers in order to improve the storage life, processability, resistance to pressure, mildewproofing and antiseptic properties, antistatic properties and coating property thereof.

Table 4 Characteristics of silver halide grains contained in emulsions Em-A' to Em-O'

	Layer in which emulsion is used	Grain shape	Av. ESD ( $\mu\text{m}$ )	Av. ECD ( $\mu\text{m}$ ) COV (%)	Av. thick-ness ( $\mu\text{m}$ ) COV (%)	Av. aspect ratio	Ratio of tabular grains: * (%)	Thick-ness of core portion ( $\mu\text{m}$ )	Tree ring structure in core portion	Number of dislocation line per grain
Em-A'	High-speed R-sens. layer	(111) main plane tabular grain	0.95	2.20/32	0.12/14	18	97	0.09	absent	20
Em-B'	Medium-speed R-sens. layer	(111) main plane tabular grain	0.69	1.30/35	0.10/15	13	98	0.07	absent	15
Em-C'	Low-speed R-sens. layer	(111) main plane tabular grain	0.48	0.89/17	0.09/12	10	99	-	-	10
Em-D'	Low speed R-sens. layer	(111) main plane tabular grain	0.31	0.40/20	0.09/9.3	4.5	98	-	-	10
Em-E'	Layer for donating interimage effect to R-sens. layer	(111) main plane tabular grain	0.78	1.38/24	0.15/13	9.2	97	0.12	present	20
Em-F'	High-speed G-sens. layer	(111) main plane tabular grain	1.00	2.40/33	0.13/14	19	99	0.09	absent	20
Em-G'	Medium-speed G-sens. layer	(111) main plane tabular grain	0.74	1.64/34	0.10/15	16	96	0.07	absent	15
Em-H'	High- and low-speed G-sens. layer	(111) main plane tabular grain	0.74	1.39/25	0.14/11	9.9	98	0.12	present	20
Em-I'	Low speed G-sens. layer	(111) main plane tabular grain	0.55	0.79/30	0.14/13	5.5	97	0.11	present	30
Em-J'	Low speed G-sens. layer	(111) main plane tabular grain	0.44	0.53/30	0.17/18	3.2	97	0.13	present	20
Em-K'	High-speed B-sens. layer	(111) main plane tabular grain	1.60	3.00/25	0.31/21	10	99	0.16	present	15
Em-L'	High-speed B-sens. layer	(111) main plane tabular grain	1.30	2.20/24	0.34/22	7	98	0.14	present	20
Em-M'	Low-speed B-sens. layer	(111) main plane tabular grain	0.81	1.10/30	0.23/18	4.7	97	0.13	present	20
Em-N'	Low-speed B-sens. layer	(111) main plane tabular grain	0.40	0.55/32	0.13/16	4.6	96	0.11	present	20
Em-O'	Low-speed B-sens. layer	(100) main plane cubic grain	0.21	0.21/20	0.21/20	1	-	-	-	-

\* Ratio of tabular grains = Ratio occupied by tabular grains to the total projected area

R-sens. = Red-sensitive; G-sens. = Green-sensitive; B-sens. = Blue-sensitive; Av. ESD = Average equivalent sphere diameter; Av. ECD = Average equivalent circle diameter; COV = Coefficient of variation; Av. thickness = Average thickness; Av. aspect ratio = Average aspect ratio

Table 5 Composition structure of silver halide grains contained in emulsions Em-A' to Em-O'

	Layer in which emulsion is used	Characteristics of grains occupying 70% or more of the total projected area	Silver amount ratio in grain structure (%) and halogen composition (from center of grain) The number in < > is halogen composition in epitaxial junction portion
Em-A'	High-speed R-sens. layer	(111) main plane tabular grain	(11%)AgBr/(35%)AgBr97I3/(18%)AgBr/(9%)AgBr62I38/(27%)AgBr
Em-B'	Medium-speed R-sens. layer	(111) main plane tabular grain	(7%)AgBr/(31%)AgBr97I3/(16%)AgBr/(12%)AgBr62I38/(34%)AgBr
Em-C'	Low-speed R-sens. layer	(111) main plane tabular grain	(1%)AgBr/(77%)AgBr99I1/(9%)AgBr95I5/(13%)AgBr63Cl35I2
Em-D'	Low speed R-sens. layer	(111) main plane tabular grain	(57%)AgBr/(14%)AgBr96I4/(29%)AgBr57Cl41I2
Em-E'	Layer for donating interimage effect to R-sens. layer	(111) main plane tabular grain	(13%)AgBr/(36%)AgBr97I3/(7%)AgBr/(11%)AgBr62I38/(33%)AgBr
Em-F'	High-speed G-sens. layer	(111) main plane tabular grain	(11%)AgBr/(35%)AgBr97I3/(18%)AgBr/(4%)AgI/(32%)AgBr
Em-G'	Medium-speed G-sens. layer	(111) main plane tabular grain	(7%)AgBr/(31%)AgBr97I3/(15%)AgBr/(14%)AgBr62I38/(33%)AgBr
Em-H'	High- and low-speed G-sens. layer	(111) main plane tabular grain	(14%)AgBr/(36%)AgBr97I3/(7%)AgBr/(11%)AgBr62I38/(32%)AgBr
Em-I'	Low speed G-sens. layer	(111) main plane tabular grain	(15%)AgBr/(44%)AgBr97I3/(11%)AgBr/(5%)AgI/(25%)AgBr
Em-J'	Low speed G-sens. layer	(111) main plane tabular grain	(60%)AgBr/(2%)AgI/(38%)AgBr
Em-K'	High-speed B-sens. layer	(111) main plane tabular grain	(68%)AgBr93I7/(21%)AgBr/(1%)AgI/(10%)AgBr
Em-L'	High-speed B-sens. layer	(111) main plane tabular grain	(8%)AgBr/(10%)AgBr95I5/(52%)AgBr93I7/(11%)AgBr/(2%)AgI/(17%)AgBr
Em-M'	Low-speed B-sens. layer	(111) main plane tabular grain	(12%)AgBr/(43%)AgBr90I10/(14%)AgBr/(2%)AgI/(29%)AgBr
Em-N'	Low-speed B-sens. layer	(111) main plane tabular grain	(58%)AgBr/(4%)AgI/(38%)AgBr
Em-O'	Low-speed B-sens. layer	(100) main plane cubic grain	(6%)AgBr/(94%)AgBr96I4

R-sens. = Red-sensitive; G-sens. = Green-sensitive; B-sens. = Blue-sensitive

Table 7 Sensitizing dye and dopant used in emulsions Em-A' to Em-O'

	Layer in which emulsion is used	Sensitizing dye	Dopant
Em-A'	High-speed R-sens. layer	1, 3, and 14	K <sub>2</sub> IrCl <sub>6</sub> , and K <sub>4</sub> Fe(CN) <sub>6</sub>
Em-B'	Medium-speed R-sens. layer	1, 2, and 3	K <sub>2</sub> IrCl <sub>6</sub> , K <sub>2</sub> IrCl <sub>5</sub> (H <sub>2</sub> O), and K <sub>4</sub> Ru(CN) <sub>6</sub>
Em-C'	Low-speed R-sens. layer	2, 3, and 14	K <sub>2</sub> IrCl <sub>6</sub> , and K <sub>4</sub> Fe(CN) <sub>6</sub>
Em-D'	Low speed R-sens. layer	2, 3 and 14	K <sub>2</sub> IrCl <sub>6</sub> , and K <sub>4</sub> Fe(CN) <sub>6</sub>
Em-E'	Layer for donating interimage effect to R-sens. layer	7 and 8	K <sub>4</sub> Fe(CN) <sub>6</sub>
Em-F'	High-speed G-sens. layer	5, 6, and 8	K <sub>4</sub> Ru(CN) <sub>6</sub>
Em-G'	Medium-speed G-sens. layer	5, 6, and 8	K <sub>2</sub> IrCl <sub>6</sub> , and K <sub>4</sub> Fe(CN) <sub>6</sub>
Em-H'	High- and low-speed G-sens. layer	4, 5, 6, 8, and 13	K <sub>2</sub> IrCl <sub>6</sub> , and K <sub>4</sub> Fe(CN) <sub>6</sub>
Em-I'	Low speed G-sens. layer	4, 5, and 6	K <sub>2</sub> IrCl <sub>6</sub>
Em-J'	Low speed G-sens. layer	6, 8, and 14	K <sub>2</sub> IrCl <sub>6</sub> , and K <sub>4</sub> Fe(CN) <sub>6</sub>
Em-K'	High-speed B-sens. layer	16	—
Em-L'	High-speed B-sens. layer	9	—
Em-M'	Low-speed B-sens. layer	16	—
Em-N'	Low-speed B-sens. layer	9 and 15	—
Em-O'	Low-speed B-sens. layer	12 and 15	K <sub>2</sub> IrCl <sub>6</sub>

R-sens. = Red-sensitive; G-sens. = Green-sensitive; B-sens. = Blue-sensitive

Table 6 Characteristics of silver halide grains contained in emulsions Em-A' to Em-O'

	Layer in which emulsion was used	Av. silver iodide content (mol%)/Inter-grain COV (%)	Grain surface silver iodide content (mol%)	Average silver chloride content (mol%)/Inter-grain COV (%)	Grain surface silver chloride content (mol%)	Twin plane distance ( $\mu\text{m}$ ) COV (%)	(100) plane ratio to side faces	Ratio in number of grains satisfying the requirement A below to the total grains
Em-A'	High-speed R-sens. layer	4.5/10	3.90	0	0	0.011/30	20	55
Em-B'	Medium-speed R-sens. layer	5.5/11	5.00	0	0	0.010/30	30	75
Em-C'	Low-speed R-sens. layer	1.5/10	3.70	4.7/8.0	16	0.010/31	25	—
Em-D'	Low speed R-sens. layer	1.1/11	5.00	12/9.0	23	0.009/29	25	—
Em-E'	Layer for donating interimage effect to R-sens. layer	5.3/10	5.90	0	0	0.012/30	35	20
Em-F'	High-speed G-sens. layer	5.1/10	3.90	0	0	0.012/30	20	60
Em-G'	Medium-speed G-sens. layer	6.3/13	5.60	0	0	0.010/30	30	65
Em-H'	High- and low-speed G-sens. layer	5.3/14	5.97	0	0	0.011/30	30	25
Em-I'	Low speed G-sens. layer	6.3/12	7.39	0	0	0.016/32	20	15
Em-J'	Low speed G-sens. layer	2.0/14	5.68	0	0	0.016/32	35	18
Em-K'	High-speed B-sens. layer	5.8/7.0	3.88	0	0	0.010/29	40	25
Em-L'	High-speed B-sens. layer	6.1/8.0	5.50	0	0	0.017/33	20	20
Em-M'	Low-speed B-sens. layer	6.3/9.0	1.90	0	0	0.019/30	30	15
Em-N'	Low-speed B-sens. layer	4.0/10	5.50	0	0	0.020/31	30	20
Em-O'	Low-speed B-sens. layer	3.8/9.0	4.50	0	0	—	—	—

Requirement A: Consisting of silver iodobromide or silver chloriodobromide grains each having {111} planes as main planes, equivalent circle diameter of  $1.0\mu\text{m}$  or more, grain thickness of  $0.15\mu\text{m}$  or less, a core portion consisting of silver iodobromide having a thickness of  $0.1\mu\text{m}$  or less without a tree ring structure and 10 or more dislocation lines.

R-sens. = Red-sensitive; G-sens. = Green-sensitive; B-sens. = Blue-sensitive; COV = Coefficient of variation



The emulsions contained the optimum amount of spectral sensitizing dye listed in Table 7, and were subjected to gold sensitization, sulfur sensitization and selenium sensitization optimally.

5           The above silver halide color photosensitive material is regarded as sample 301.

(Preparation of Samples 302 to 313)

10           Samples 302 to 313 were prepared in the same manner as sample 301, except that the compound of the present invention was added to the sixth, eleventh, and fourteenth layers of sample 301, as shown in Table 8.

          Samples 301 to 313 were exposed for 1/100 second through a gelatin filter SC-39 manufactured by Fuji Photo Film Co., Ltd. and a continuous wedge.

15           The sample after being exposed was processed by the same method as described in Example 1.

          The speed and graininess of the red-sensitive layer, green-sensitive layer and blue-sensitive layer were determined using the method described in Example 1.

Table 8

Sample No.	Compound of general formula (M) or general formula (C)	Addition amount (per mol of Ag $\times 10^{-3}$ mol)			Speed			Graininess		
		6th layer	11th layer	14th layer	R layer	G layer	B layer	R layer	G layer	B layer
301 (Comp.)	—	—	—	—	0.00	0.00	0.00	100	100	100
302 (Comp.)	Comparative compound A	14	14	12	+0.03	+0.03	+0.03	101	101	102
303 (Inv.)	(86)	14	14	12	+0.06	+0.05	+0.05	101	101	101
304 (Inv.)	(88)	14	14	12	+0.07	+0.07	+0.06	100	101	101
305 (Inv.)	(93)	14	14	12	+0.11	+0.10	+0.08	101	100	100
306 (Inv.)	(100)	14	14	12	+0.10	+0.09	+0.08	101	101	101
307 (Inv.)	(101)	14	14	12	+0.09	+0.08	+0.07	101	100	100
308 (Inv.)	(106)	14	14	12	+0.09	+0.08	+0.07	101	101	100
309 (Inv.)	(89)	14	14	12	+0.09	+0.08	+0.07	101	101	101
310 (Inv.)	(97)	14	14	12	+0.08	+0.07	+0.06	102	100	101
311 (Inv.)	(104)	14	14	12	+0.08	+0.07	+0.06	102	102	101
312 (Inv.)	(110)	14	14	12	+0.11	+0.10	+0.08	102	101	102
313 (Inv.)	(111)	14	14	12	+0.07	+0.07	+0.06	101	101	101

Note: R layer = Red-sensitive layer;

G layer = Blue-sensitive layer;

B layer = Blue-sensitive layer

It is apparent from the above results that the method of the present invention is excellent in obtaining a high quality image. This is made possible by increasing the speed of the photosensitive material without deteriorating the graininess.

Additional advantages and modifications will readily occur to those skilled in the art. Therefore, the invention in its broader aspects is not limited to the specific details and representative embodiments shown and described herein. Accordingly, various modifications may be made without departing from the spirit or scope of the general inventive concept as defined by the appended claims and their equivalents.